

Experimental investigation of a DISI production engine fuelled with methanol, ethanol, butanol and iso-stoichiometric alcohol blends

Author, co-author (Do NOT enter this information. It will be pulled from participant tab in MyTechZone)

Affiliation (Do NOT enter this information. It will be pulled from participant tab in MyTechZone)

Abstract

Stricter CO₂ and emissions regulations are pushing spark ignition engines more and more towards downsizing, enabled through direct injection and turbocharging. The advantages which come with direct injection, such as increased charge density and an elevated knock resistance, are even more pronounced when using low carbon number alcohols instead of gasoline. This is mainly due to the higher heat of vaporization and the lower air-to-fuel ratio of light alcohols such as methanol, ethanol and butanol. These alcohols are also attractive alternatives to gasoline because they can be produced from renewable resources. Because they are liquid, they can be easily stored in a vehicle.

In this respect, the performance and engine-out emissions (NO_x, CO, HC and PM) of methanol, ethanol and butanol were examined on a 4 cylinder 2.4 DI production engine and are compared with those on neat gasoline. Additionally, measurements were done for E85 and a methanol-gasoline blend with the same air-to-fuel ratio as E85 because this 'iso-stoichiometric' methanol-gasoline blend shows very few differences in physical properties to E85 and has the potential to be used as 'drop-in' fuel for flex-fuel vehicles. It is shown that the brake thermal efficiency when running on alcohol fuels is significantly better than with gasoline while emitting fewer emissions. In a knock limited case for gasoline, the brake thermal efficiency on methanol was more than 5 percentage points better than on gasoline. The engine test results also confirm that, from an engine control point of view, the 'iso-stoichiometric' methanol-gasoline blend can indeed be used as a 'drop-in' fuel for E85.

Introduction

Stricter CO₂ and emissions regulations are pushing spark ignition engines more and more towards downsizing resulting in a stronger demand of the transport sector for higher octane gasoline. In the United States, the Corporate Average Fuel Economy (CAFE) standards are projected to result in an average industry fleetwide level

of 163 g/mile (101 g/km) of CO₂ in 2025, which is equivalent to 54.5 mpg [1]. For light-duty vehicles in the European Union, manufacturers are obliged to ensure that their new car fleet does not emit more than an average of 130 g/km of CO₂ by 2015 and 95 g/km by 2021 [2]. A possible solution could be to look at an alternative drivetrain such as an electric motor using batteries or a hydrogen fuel cell. These drivetrains are already widely investigated and electric vehicles are already in use. Nevertheless, the low volumetric energy density of batteries and hydrogen provide these vehicles with a limited range compared to conventional vehicles with an internal combustion engine (ICE). Additionally, a transition to either hydrogen vehicles or battery electric vehicles will result in increases in both vehicle and infrastructure costs making it questionable if they will become competitive with vehicles running on liquid fuels in the near future [3].

It is anticipated that alternative fuels will play an important role in reducing CO₂ emissions. In the United States, the U.S. Renewable Fuel Standard (RFS2) requires the use of biofuels to be increased to a total of 36 billion ethanol-equivalent gallons per year by 2022. RFS2 limits corn-based ethanol to 15 billion gallons and requires the use of 1 billion gallons of biomass-based diesel, leaving 20 billion gallons to come from other advanced biofuels [4]. Likewise, the European Union has also set a target of 10% of transport fuel to be from renewable sources by 2020 [5].

Alcohol fuels

Methanol, ethanol and butanol

Liquid alcohols such as methanol, ethanol and butanol which can be produced in a renewable way could be presented as promising fossil fuel replacements [6-8]. Light alcohols can be used in internal combustion engines. Flex-fuel operation of spark-ignition engines on gasoline and different alcohols is straightforward using modern control technology and can be achieved with very low on-cost modifications to the fuel system [9]. Because they are liquid, they can be easily stored in a vehicle [10]. They are also miscible with gasoline which enables a soft start to an alternative fuel economy

[11]. As a result, they are already used as blend-in fuels (e.g. E10) for production cars in limited concentrations.

Renewable ethanol can be made from biomass such as corn or sugarcane. This is often referred to as bio-ethanol. For now, bio-ethanol has the upper hand when it comes to non-petroleum-derived transportation energy. Despite of the projected growth, bio-ethanol is not considered to be viable in the long term as a substitute for fossil fuels, due to the biomass limit [9]. This biomass limit is different for each country, and depends on the amount of biomass that can be grown, the amount of energy required by the country, any impact of land-use change that may arise, and limits set by any impact on the food chain [12], [13]. It has been estimated that this limits the potential of biofuels to about 20% of the energy demand in 2050 [3].

Synthetic fuels, sometimes described as ‘electrofuels’ [3, 14-19], are not constrained by a biomass limit and could become more and more important in the future. These energy carriers are synthesized from CO₂ and water using renewable energy. In other words, CO₂ is captured and combined with renewable hydrogen to form a liquid hydrogen carrier. This results in a closed CO₂ cycle. Methanol is the most energetically efficient liquid electrofuel that can be synthesized using this approach [3]. Next to this approach, methanol can also be produced from a variety of fossil fuels such as coal and natural gas and from renewable sources (e.g. gasification of wood, agricultural by-products and municipal waste).

A disadvantage of methanol and ethanol is that the energy density is significantly lower compared to gasoline (see Table 1) which negatively impacts the volumetric fuel economy and, as a result, also the vehicle range. Ethanol and methanol are also hydrophilic which could give problems when being transported via pipelines [20]. Butanol, on the other hand, is much less soluble in water, does not tend to phase separate in the presence of water and gasoline and benefits from an energy density which is closer to the energy density of gasoline. The energy density of butanol is only 15% less than that of gasoline. As in the case of methanol and ethanol, butanol can be produced from renewable sources. However, since renewable butanol is mainly made from biomass, it also has a biomass limit.

Butanol has a four-carbon structure so different isomers exist based on the location of the hydroxyl group (OH group). The different structures of butanol isomers have a direct impact on the physical properties. The different isomers are called n-butanol (1-butanol), sec-butanol, tert-butanol and isobutanol and the chemical structure is shown in Figure 1. Sec-butanol is not considered a potential alternative engine fuel due to its low motor octane number of 32. Tert-butanol is not considered to be used as an alternative fuel at higher volumetric concentrations, due to its high melting point. 1-butanol and isobutanol have physical properties closer to gasoline and could therefore be considered a potential alternative fuel. In this study, only isobutanol was used because of the higher octane number which is close to the octane number of methanol and ethanol. From here on, isobutanol will be simply called butanol.

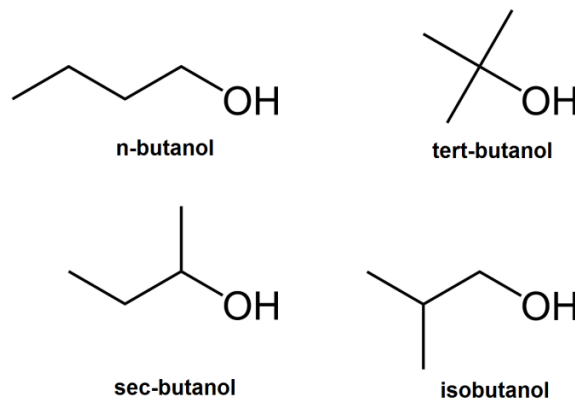


Figure 1 – Chemical structure of butanol isomers

Ternary blends of methanol, ethanol and gasoline

Turner et al. [12, 21] presented the concept of ternary blends of gasoline, ethanol and methanol in which the stoichiometric air-to-fuel ratio is controlled to be the same as that of conventional E85 alcohol-based fuel. In fact, starting from any binary gasoline–ethanol mixture, a ternary blend of gasoline, ethanol and methanol can be devised in which the fraction of each component is chosen to yield the same stoichiometric air to fuel ratio. In Figure 2, the concept of these ternary blends is shown for equivalent ‘E85’ blends. On the right side of Figure 2, the composition of normal E85 can be seen (85 v/v% ethanol and 15 v/v% gasoline). On the left side of Fig. 1, the binary mixture of gasoline and methanol is shown in which all the ethanol is replaced with gasoline and methanol. This results in a M56 blend (56 v/v% methanol and 44 v/v% gasoline). In between these two blends, any iso-stoichiometric ternary blend can be determined by drawing a vertical line in Fig. 1 and reading the blend ratios on the left axis of the figure (for example the yellow dotted line in Fig. 1).

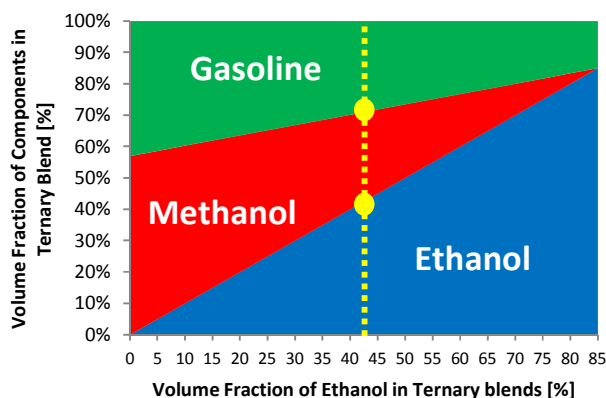


Figure 2: iso-stoichiometric GEM blends equivalent to conventional E85 [21].

Turner et al. [21] found that all the possible iso-stoichiometric ternary blends starting from a binary blend of gasoline and ethanol have, beside the same AFR, essentially identical volumetric energy content, constant octane numbers and constant latent heat. This opens the possibility to use these ternary blends as drop-in fuels for flex-fuel vehicles without the danger of upsetting the on-board diagnostics of

the engine management system. If the methanol used is of a renewable and energy-secure nature then, for a fixed volume of ethanol in the fuel pool dependent on the biomass limit, an increased level of renewability and energy security is achieved. This overall situation is made possible by the fact that there are more E85/flex-fuel vehicles in existence than can currently be serviced by the E85 fuel supply chain. Turner et al. [21] tested the drop-in ability of the iso-stoichiometric GEM blends in two flex-fuel vehicles. During vehicle testing, the hypothesis that iso-stoichiometric GEM blends can function as drop-in alternatives to binary ethanol–gasoline blends has been confirmed. This hypothesis has also been tested by Sileghem et al. [22] on a flex fuel PFI production spark ignition engine with positive results. It should be noted that this drop-in ability did not yet include necessary tests for long-term durability, materials compatibility and metal corrosion (both ethanol and methanol being known to be more aggressive to some polymers and light metals than gasoline).

With existing commercial E85 fuels, the ethanol content is decreased to levels close to 70% in order to maintain cold startability. As methanol is not as hard to start on as ethanol, a year-round fixed blend ratio is therefore a possibility. This means that GEM blends could effectively extend gasoline displacement during winter months. Other benefits of the GEM-blends are the potential economic advantage. Turner et al. [21] showed that with wholesale prices of \$3.11, \$2.30 and \$1.11 per US gallon for gasoline, ethanol and methanol respectively, the price of the blends can be made significantly lower than gasoline on an energy basis. A reduction in motoring costs, by a reduction in relative price of the fuel versus gasoline, could be achieved at these wholesale prices using ternary blends containing more than 25% by volume of methanol.

In this study, only E85 and the equivalent methanol-gasoline blend M56 are tested. The variation between the different blends is not expected to be substantial according to the results of Turner et al. [21] on a flex fuel vehicle and Sileghem et al. [22] on a PFI engine. In this study a direct injected engine is used and as a result, special attention will go to the injection parameters.

Alcohol vs. gasoline

Alcohols exhibit several favorable properties as a fuel for spark-ignition engines with the potential to increase engine performance and efficiency compared to gasoline. These properties are becoming more pronounced as the carbon count in the alcohol decreases (with the exception of the octane numbers, see Table 1). In other words, these interesting properties are more marked with methanol (being the lightest alcohol) and thus the potential for increase in power and efficiency is highest for this fuel while this is to a lesser extent the case for ethanol and butanol.

In Table 1, the properties of gasoline (EEE Certification fuel), methanol, ethanol and butanol relevant to their use in internal combustion engines are summarized. Only the laminar burning velocity of butanol could not be located in the literature for the same conditions as for methanol, ethanol and gasoline [23, 24].
[Table 1 -Properties of typical gasoline, methanol, ethanol and butanol relevant to internal combustion engines.](#)

Property	Gasoline EEE	Methanol	Ethanol	Butanol
Chemical formula	Various	CH ₃ OH	C ₂ H ₅ OH	C ₄ H ₉ OH

Oxygen Content by mass (%)	0	49.93	34.73	21.58
Density at NTP (kg/l)	0.742	0.79	0.79	0.802
Lower heating value (MJ/kg)	42.74	20.09	26.95	33.08
Volumetric Energy Content (MJ/l)	31.71	15.90	21.29	26.53
Stoichiometric AFR (kg/kg)	14.6	6.5	9.0	11.2
Energy per unit mass of air (MJ/kg)	2.93	3.09	2.99	2.95
Research Octane Number (RON)	97.1	109	109	113
Motor Octane Number (MON)	88.7	88.6	98	94
Sensitivity (RON-MON)	8.4	20.40	11	19
Boiling point at 1 bar (°C)	25-215	65	79	108
Heat of vaporization (kJ/kg)	~350	1100	838	566
Reid vapour pressure (psi)	9.00	4.60	2.30	0.49
Mole ratio of products to reactants ^a	0.933	1.061	1.065	1.067
Laminar burning velocity at NTP, $\lambda = 1$ (cm/s)	33.0	40.0	38.5	-
Specific CO ₂ emissions (g/MJ)	74.15	68.44	70.99	71.79
^a Includes atmospheric nitrogen. NTP: normal temperature (293K) and pressure (101325 Pa)				

Due to a high heat of vaporization in combination with the low stoichiometric air to fuel ratio, the intake charge is cooled more for alcohol fuels as the injected fuel evaporates. This effect can be exploited even more with direct injection and provides an increased charge density. The resulting lower in-cylinder temperatures will also have a positive effect on NO_x-emissions, heat losses and knock resistance. Additionally to the elevated knock resistance due to the cooling effect, there is also a chemical effect. These two effects result in high octane numbers for the alcohol fuels considered in this study. This opens opportunities for increased power and efficiency by applying higher compression ratios, optimal spark timing and aggressive downsizing. In combination with aggressive downsizing significant efficiency gains can be achieved without the need for using a rich mixture at high load. Finally, due to the higher burning velocity of alcohols (especially methanol and ethanol) in comparison to gasoline [23, 24], the combustion is more isochoric, approaching the ideal cycle more closely. An advantage of this increased burning velocity is the potential of broadening the EGR working range.

Experimental setup

The engine used for the experimental assessment of alcohol fuels is a Hyundai 2.4L GDI engine (Theta II), a naturally aspirated, 4-cylinder, gasoline direct injection (GDI) platform used in a range of Hyundai vehicles in the United States. The main engine specifications are summarized in Table 2.

Table 2 - Specifications of the test engine

Hyundai GDI engine	
Model	Theta II
Cylinders	4
Displacement	2.36 L
Compression ratio	11.3
Bore	88 mm
Stroke	97 mm
Rated power (gasoline)	147 kW at 6300 rpm
Maximum torque (gasoline)	250 Nm at 4250 rpm

The test engine is heavily instrumented including a range of temperature and pressure probes, fuel and air flow measurement, in-cylinder pressure transducers as well as exhaust emissions probes. The engine is equipped with an Engine Control Unit (ECU) that allows for adjustment of operational parameters such as spark timing and injection parameters. For this study, a stock ECU calibration for unleaded gasoline operation with the factory engine knock detection algorithm activated was used. All tests were run with stock, early injection resulting in homogeneous charge using a closed loop feedback to tightly control air/fuel ratio to stoichiometric conditions.

Regulated emissions of carbon monoxide (CO), hydrocarbons (HC) and oxides of nitrogen (NO_x) of pre-catalyst emission samples (engine-out emissions) were measured using a Horiba MEXA7100. The raw emissions bench uses separate analyzers to determine the level of NO_x, HC, CO, CO₂, and O₂ in the exhaust stream. Using a heated sample line, exhaust is fed to an oven that houses a heated flame ionization detector (FID Model FIA-725A) and a heated chemiluminescent detector (CLD Model CLA-720MA) for HC and NO_x emissions measurements, respectively. CO is measured using cold analyzers (NDIR). The soot mass concentration in exhaust gas (PM emissions) is measured by using an AVL 483 Micro Soot Sensor.

Dynamometer data was collected for 120 seconds and cylinder pressure data for 200 engine cycles after measurements were allowed to stabilize. The dynamometer data was collected two consecutive times at each operating point. High-speed individual cylinder pressure data was taken with an AVL IndiModul system.

The graphs in the next sections include error bars that reflect the standard deviation of the results. In general this is calculated based on the standard deviation of the measured input values determined over the measurement interval. For emission measurements, additional uncertainty based on the repeatability ($\pm 1.0\%$ of the full scale range) and linearity ($\pm 1.0\%$ of the full scale range or $\pm 2.0\%$ of

measurement value, whichever is smaller) of the emission bench was added to the error based on the standard deviation of the input values.

Results and discussion

Measurements were done for pure methanol, ethanol, butanol, gasoline and two blends of alcohol and gasoline: E85 (85% v/v ethanol and 15% v/v gasoline) and M56 (56% v/v methanol and 44% v/v gasoline). The results presented in the next section were acquired during steady state operating conditions at various engine speeds and loads. The basic engine map, which prescribes injection properties and ignition timing for gasoline, was adjusted for the other fuels through fuel trims and ignition advancement in order to keep lambda equal to 1 and have MBT (Minimum spark advance for best torque) timing if possible. For knock-limited operating conditions, BLD (border line detonation) spark timing was used. Stoichiometric operation was chosen in order to maximize the conversion rate of the commonly used TWC.

Pure fuels

Performance

First, the efficiencies on pure methanol, ethanol, butanol and gasoline operation are compared at different fixed torque settings (50, 75 and 150 Nm corresponding to 2.66, 4 and 8 bar bmep) and for a range of engine speeds (1500-2000-2500-3000 rpm).

Figure 3 shows the brake thermal efficiency for the different fuels at different loads and a range of engine speeds. Notice that at high load and high rpm, it was not possible to measure on pure methanol because the stock ECU did not allow enough adjustment of the fuel trim to maintain operation at lambda equal to 1. As a result, only 1 operation point on pure methanol was measured at 150 Nm because it was not possible to measure at the same operating conditions at speeds higher than 1500 rpm.

In Figure 3 A and B, every operating point could be achieved with MBT timing as there was no knock at these lower loads. The efficiency of the different fuels behaves in a similar way as a function of engine speed. In Figure 3 C, the curve is different for gasoline because at 1500, 2000 and 2500 the ignition timing for gasoline could not be advanced until MBT timing was achieved but BLD spark timing had to be used to avoid knock. Starting with the non-knock-limited operating points, it is clear that methanol has the superior efficiency. Jung et al. [25] compared E85 to gasoline in an alternating back-to-back manner and quantified the effects which resulted in the higher brake thermal efficiency of E85. Approximately half of the improvement could be attributed to the way the heating value is measured in a combustion bomb. The remaining difference was mostly due to lower heat transfer losses. Differences in pumping work and emissions accounted for only a small fraction.

When measuring the heating value in a combustion bomb, the Heat of Vaporization of the fuel detracts from the heat release while this is not the case for the heat released during combustion in a SI engine because the fuel is already evaporated before combustion. This effect on the efficiency can be accounted for by recalculating the efficiency using the sum of the heating value and the Heat of Vaporization instead of only the heating value that is measured in a combustion bomb. In Figure 4, the 'corrected' brake thermal efficiency for a fixed torque of 75 Nm is shown. As seen on the Figure, the efficiencies of the different fuels are lower and closer to each other.

This is because of the higher Heat of Vaporization of the alcohol fuels compared to gasoline. More than half of the improvement for methanol can be attributed to this effect. For ethanol and butanol, almost the entire increase in efficiency can be attributed to this effect at 1500 rpm. Doing measurements in an alternating back-to-back manner as was done by Jung et al. [25] can help do improve the accuracy of the measurements while further optimization of the direct injection of the alcohol fuels is probably needed to fully use the charge cooling potential in flex-fuel engines.

Besides the greater charge cooling potential, alcohol fuels can have lower in-cylinder heat transfer losses due to the lower adiabatic flame temperature. The adiabatic flame temperature increase is a function of the heat released per mole and the molar specific heat of the combustion products. With same method used by Jung et al. [25] to take the effect of the Heat of Vaporization on the heat release into account, it was found that the heat released per mole of combustion products is for methanol, ethanol and butanol is lower than for gasoline. This is shown in Table 3. In Table 3, the fraction of triatomic molecules in the combustion products is also shown. Because of the higher proportion of triatomic molecules compared to gasoline, the specific heat at high temperatures is expected to be slightly higher. However, the effect of heat transfer losses could not be studied accurately enough because more engine data was needed to quantify the heat transfer losses in an engine cycle model. E.g. internal EGR and effects of fuel impingement on the metal surfaces of the cylinder and their effect on heat transfer could not be simulated with enough accuracy.

Table 3 – Heat release per mole of combustion products and percentage of triatomic molecules in combustion products for gasoline, methanol, ethanol and butanol

	Gasoline EEE	Methanol	Ethanol	Butanol
Heat released per mole of combustion products [MJ/mole]	0,0800	0,0782	0,0783	0,0787
Decrease compared to gasoline [%]	0%	2,23%	2,19%	1,72%
Percentage of triatomic molecules in combustion products [%]	25,8%	34,6%	30,6%	28,4%
Increase compared to gasoline [%]	0%	34%	19%	10%

Methanol and ethanol also have the potential of broadening the EGR working range due to the higher burning velocity. A shorter burn duration due to higher burning velocities can also have a positive impact on the efficiency [26] because of the more isochoric combustion. However, increase in combustion rate results in higher pressure rise, higher cylinder temperature, and hence, higher heat transfer loss [27]. As a result, it is expected that the effect higher burning velocity on the thermal efficiency is almost negligible.

As most of the properties of ethanol and butanol (see Table 1) are in between those of methanol and gasoline, it was expected that the

efficiency of ethanol and butanol would be in between the efficiency of methanol and gasoline as can be seen in Figure 3. For most operating points, it seems that there is a slightly better efficiency (based on the LHV) in the case of ethanol compared to butanol.

The increase in brake thermal efficiency of the three alcohol fuels becomes significant at the operating points where gasoline is knock-limited. All alcohol fuels could be run at 150 Nm without being knock-limited. For methanol, there was an improvement of 2.7 percentage points on average compared to gasoline for the non-knock-limited operating points at 50 and 75 Nm but for the knock-limited case at 150 Nm and 1500 rpm this difference increased to 5.6 percentage points with the brake thermal efficiency of methanol reaching almost 40%. This means that with the trend of downsizing and also downsizing of spark ignition engines, there is a big efficiency improvement possible with these alcohol fuels.

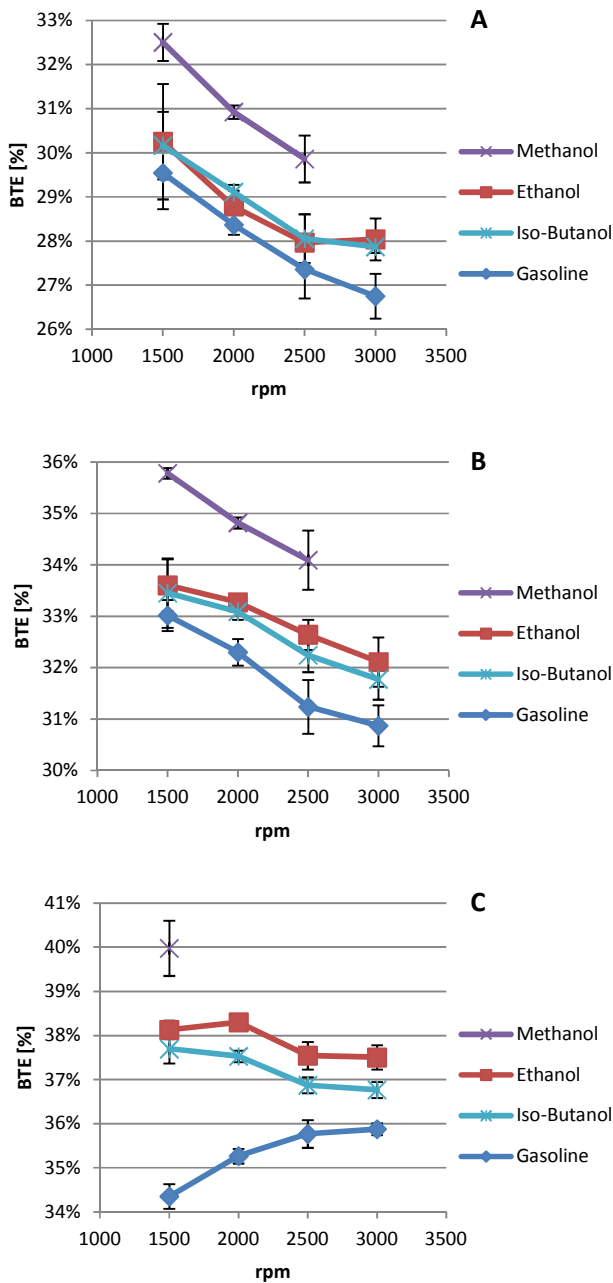


Figure 3 - Brake thermal efficiency as a function of engine speed for different fixed brake torques of 50 Nm (A), 75 Nm (B) and 150 Nm (C).

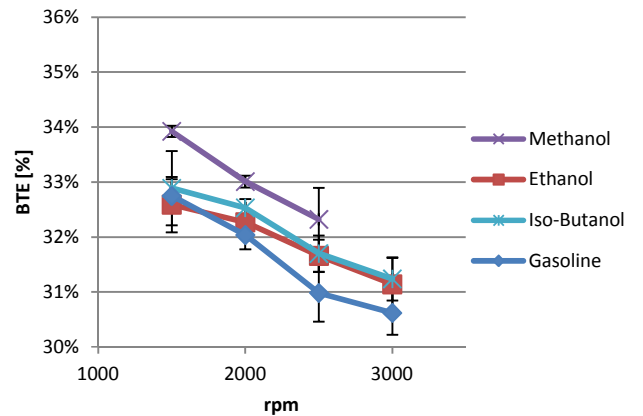


Figure 4 – Corrected brake thermal efficiency as a function of engine speed for different fixed brake torque of 75 Nm.

Efficiency is closely related to the CO₂ emissions. As can be seen in Table 1, the specific CO₂ emissions are the lowest for methanol, followed by ethanol, butanol and gasoline. Even if the efficiency of the four different fuels was the same, methanol, ethanol and butanol would emit lower CO₂ emissions than gasoline. Together with the increased efficiency, it is clear that a large CO₂ emission reduction is possible as is shown in Figure 5. Figure 5 shows the CO₂ emissions of the different fuels for the different fixed torques as a function of engine speed. As expected, the biggest drop in CO₂ emissions is at 150 Nm and 1500 rpm in the case of methanol. There is a decrease of 20.7 % compared to gasoline. These emissions are only engine out CO₂ emissions. If you take into account that methanol, ethanol and butanol can be produced from renewable resources, the well to wheel CO₂ emissions would decrease even more compared to gasoline.

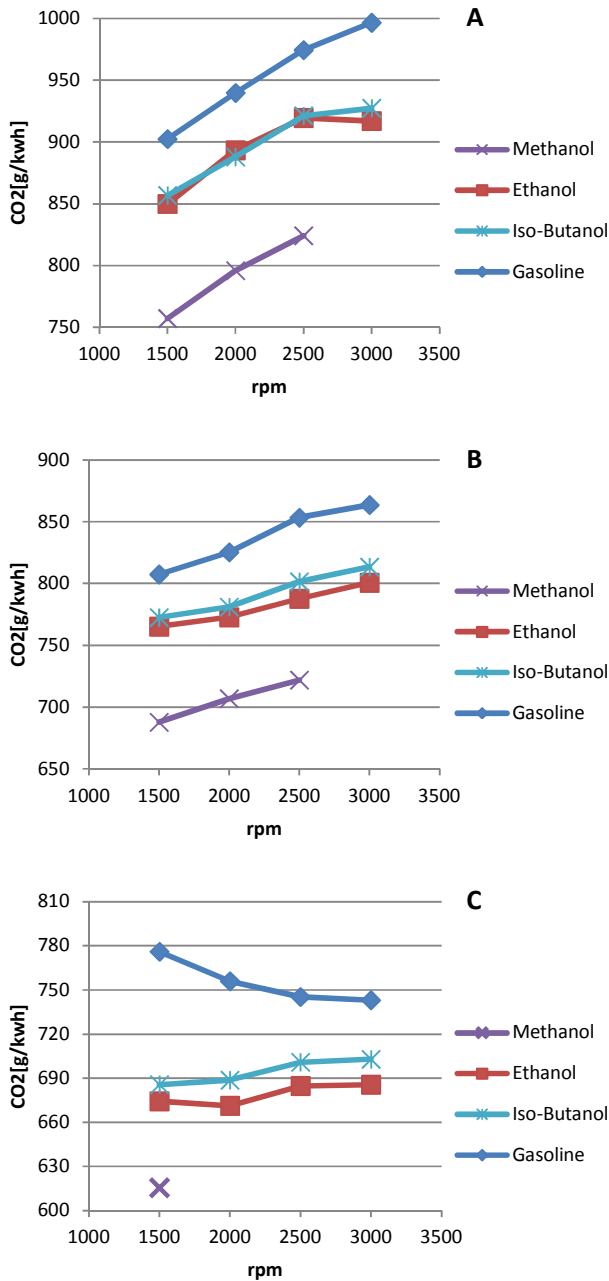


Figure 5 – CO₂ emissions as a function of engine speed for different fixed brake torques of 50 Nm (A), 75 Nm (B) and 150 Nm (C).

Based on the properties of methanol, ethanol and butanol (high heat of vaporization and low air to fuel ratio) and given the fact that the efficiency for these alcohol fuels is higher than the efficiency of gasoline, one could expect that the exhaust temperature would be the lowest for methanol, followed by ethanol and butanol, and the highest for gasoline. In Figure 6, the exhaust temperature for the four fuels is shown for a torque load of 75 Nm as a function of the engine speed. As expected, the exhaust temperature of gasoline is the highest with a 20-30 K increase compared to the alcohol fuels. The exhaust temperatures of methanol, ethanol and butanol are, on the other hand, very similar. The temperature can change due to several factors. For example, the exhaust temperature depends on the amount of fuel, air

and dilution (internal EGR) in the cylinder. Because of the different properties of the fuels, the throttle position was not the same at the same load for every fuel and the interaction of the fuel spray with the air could have an effect on the gas dynamics changing the amount of dilution. Another possible reason is that the spray of the direct fuel injection is not yet optimized to take full advantage of the possible charge cooling of these fuels. As a result, a relatively big fraction of the vaporization heat could be taken from the cylinder walls and piston. Using the cylinder pressure traces of the different measurements in simulation models can help to point out which effects are decisive.

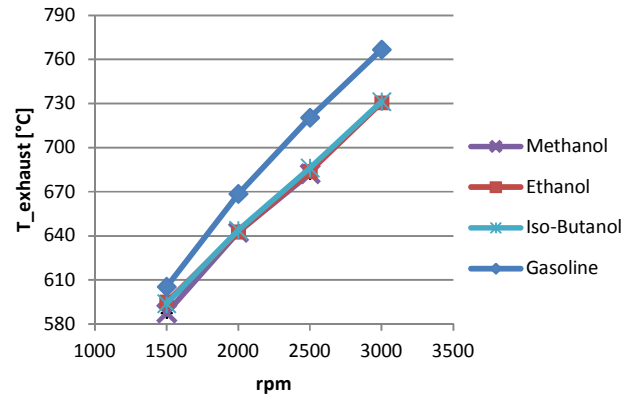


Figure 6 – Exhaust temperature as a function of engine speed for a fixed brake torque of 75 Nm.

Pollutant emissions

In this section, the trends of NO_x, CO, UHC and PM emissions are shown and discussed for the pure fuels: methanol, ethanol, butanol and gasoline. Emissions of unburned fuel were measured using flame ionization detectors. It has been reported that using the flame ionization detector technique might lead to an underestimation of the total unburned hydrocarbons of alcohol fuels. The reason for this is that oxygenated species are commonly found in the exhaust gases of alcohol engines but the reaction time for oxygenated hydrocarbons is impracticably long for flame ionization detectors and thus realistic values are not possible. However, the UHC can be corrected using a response factor. The corrected UHC emissions are calculated using the uncorrected UHC measurement from the FID measurement and a response factor unique to each fuel.

Response factors for ethanol and the butanol were calculated from the study done by Wallner [28]. Wallner developed a correlation for response factors based on emissions measurement on ethanol-gasoline and butanol-gasoline blends performed with a standard raw emissions bench with FID as well as with an emissions bench with Fourier transform infrared spectroscopy (FTIR). This correlation is solely based on volumetric alcohol content and carbon count of the alcohol fuel used for blending. This correlation was also tested for data of methanol-gasoline blends measured by Yanju et al. [29] which included operating conditions for blend levels of 10 vol%, 20 vol% and 85 vol% at various speeds and loads but no satisfying agreement was found. As a result, for the response factors of methanol, data from the study of Yanju et al. [29] was used instead of the correlation developed by Wallner et al. [28]. In Figure 7, the

response factors derived from the data are shown together with a fitted trend line which made it possible to estimate the response factor at 100% methanol. The equation of the trendline was also used to calculate the response factor for the M56 GEM fuel to correct the UHC emissions of M56 in the next section. The data provided by Yanju et al. [29] was the only data available in literature. When interpreting the corrected UHC emissions results, it is important to keep in mind that the methanol response factors were based on a very limited set of data which has not been evaluated by other measurements.

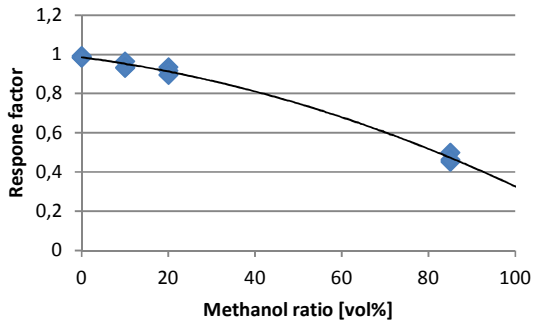


Figure 7 – Response factor for UHC emissions of methanol

In Figure 8, the NO_x emissions are shown for the four different fuels at a fixed load of 75 Nm and a range of engine speeds. The highest NO_x emissions are clearly on gasoline and the lowest NO_x emissions are on methanol. The NO_x emissions of ethanol and butanol are in between gasoline and methanol. The lower combustion temperature of the alcohol fuels is responsible for the lower NO_x emissions since most NO_x is produced by the thermal mechanism which is very dependent on temperature. The lower NO_x emissions at lower engine speeds might be caused by elevated levels of internal EGR given the vacuum in the intake due to throttling at lower engine speeds. It is remarkable that the maximum difference in NO_x emissions between the three alcohol fuels is around 3.8 g/kWh and that the difference between butanol and gasoline is 6.15 g/kWh on average. In other words, the NO_x emissions of the three alcohol fuels do not differ a lot while there is a big increase for the gasoline NO_x emissions. This could be linked to the very similar exhaust temperatures of the alcohol fuels as discussed earlier as the NO_x mechanism is very dependent on temperature.

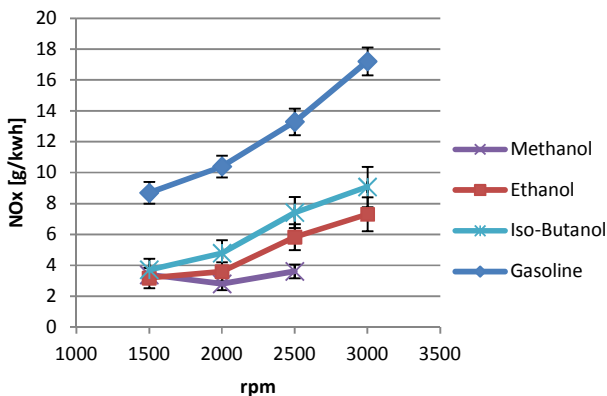


Figure 8 – NO_x emissions as a function of engine speed for a fixed brake torque of 75 Nm.

The engine-out CO and UHC emissions for the different fuels are compared in Figure 9 and Figure 10 respectively for a load of 75 Nm. In Figure 10 A, the uncorrected UHC emissions are shown and in Figure 10 B, the UHC emissions are corrected with response factors calculated as discussed earlier. The CO and UHC emissions of alcohol fuels could be lower than gasoline due to the oxygenated nature of alcohols which might cause a more complete combustion [30]. In Figure 9, it seems that gasoline has the highest CO emissions while there is no clear trend for methanol, ethanol and butanol.

When looking at the uncorrected UHC emissions of the different fuels in Figure 10 A, there seems to be a clear trend. Methanol has the lowest UHC emissions, followed by ethanol, butanol and gasoline. This trend could be explained by the increasing oxygen content of the alcohol fuels. For the corrected emissions in Figure 10 B, this trend is still present for gasoline, ethanol and butanol but the trend is less pronounced. However, for methanol, it seems that the correction made by the response factor could be overestimated as the trend of ethanol, butanol and gasoline as a function of engine speed behaves in a more or less similar way while for methanol the decrease with increasing engine speed is much steeper. As mentioned earlier, the response factors for methanol are calculated with a very limited data set of emission measurements. More validation of the difference between the actual unburned fuel and HC emissions and the UHC emissions measured with the FID technique is therefore needed.

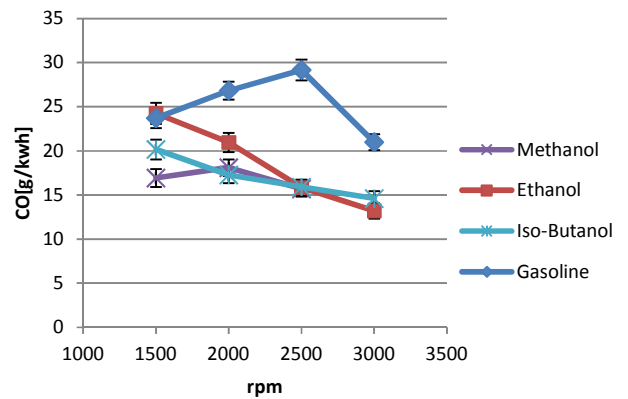


Figure 9 – CO emissions as a function of engine speed for a fixed brake torque of 75 Nm.

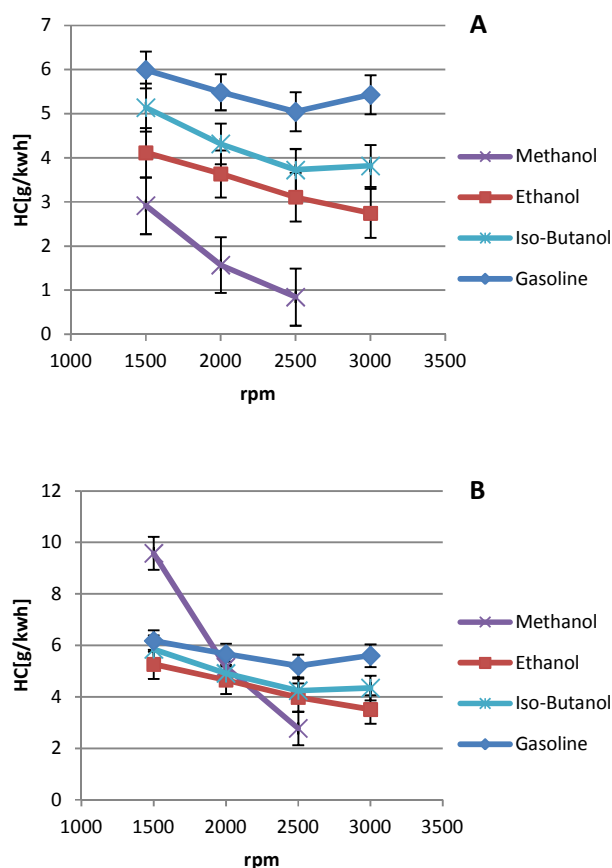


Figure 10 – Uncorrected UHC (A) and corrected UHC emissions (B) as a function of engine speed for a fixed brake torque of 75 Nm.

Finally, in Figure 11 the PM emissions are shown as a function of engine speed for a fixed torque of 75 Nm. Because of the oxygenated nature of alcohols, it is expected that the PM emissions will be lower. Additionally, it is often assumed that a methanol engine is free from particle emissions because there is no carbon-carbon bond in the molecule of methanol. However, during the combustion, soot precursors such as benzene, pyrene, etc. with carbon-carbon bonds can be formed. In Figure 11, gasoline clearly has the highest soot emissions while the trend is not completely clear for the three alcohol fuels. At lower rpm, butanol has the highest PM emissions while at higher rpm, it has the lowest emissions. This trend is not seen at the other load points, but for all the load points, it is clear that gasoline has higher soot emissions than the alcohol fuels.

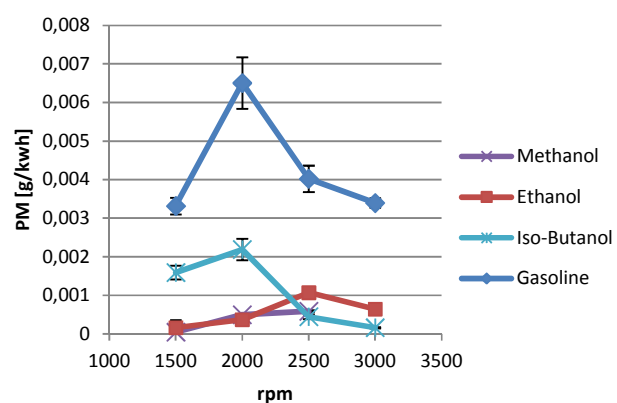


Figure 11 – PM emissions as a function of engine speed for a fixed brake torque of 75 Nm.

E85 vs. M56

In this section, we will zoom in on the difference between two iso-stoichiometric GEM blends: E85 and M56. M56 is the iso-stoichiometric blend with the maximum fraction of methanol starting from E85. Every other GEM blend that would be stoichiometric to E85 would have properties between these two blends. As a result, it is expected that the results of every other GEM blend starting from E85 would be between the results of the binary blends tested in this study.

First, measurements were done for E85 at fixed loads of 50, 75 and 150 Nm for a range of engine speeds. All parameters regarding injection (start of injection and injection pressure) and ignition were kept the same for the measurements on M56. Only very small adjustments of the throttle valve were allowed to have the same torque output with M56 as with E85. The ECU data and high-speed cylinder pressure data was used to investigate if there could be a significant difference between the combustion behavior of these two blends with very similar properties.

In Figure 12, the brake thermal efficiency for E85 and M56 is shown at different loads and a range of engine speeds. The only significant difference can be seen for a fixed torque of 150 Nm. In Figure 12 C, it is clear that at an engine speed of 2500 the error bars do not overlap. For 50 and 75 Nm, the brake thermal efficiencies are very close with overlapping error bars for each operating point. The difference in injection duration between E85 and M56 is shown in Figure 13. It can be seen that for 50 Nm and 75 Nm, the difference exceeds 1% for only one operating point. For 150 Nm, the differences are larger but still less than 3%.

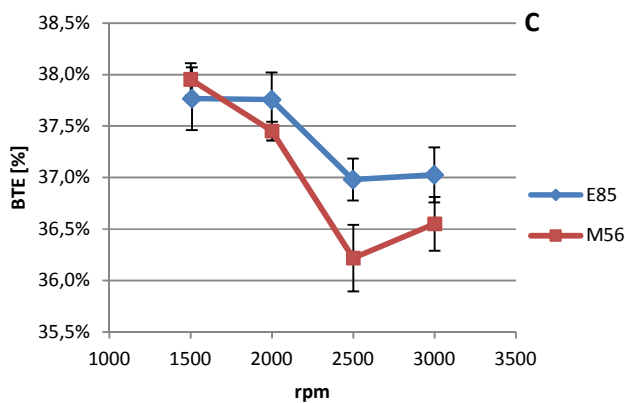
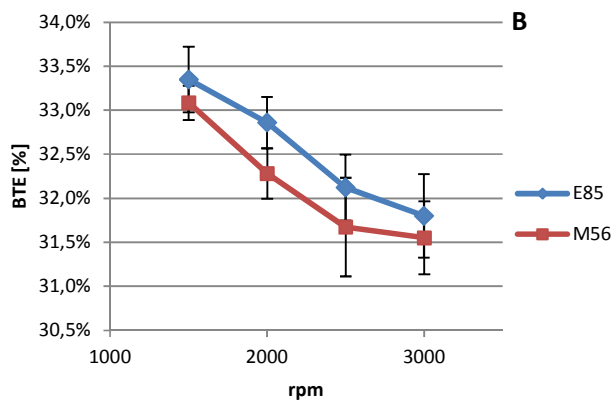
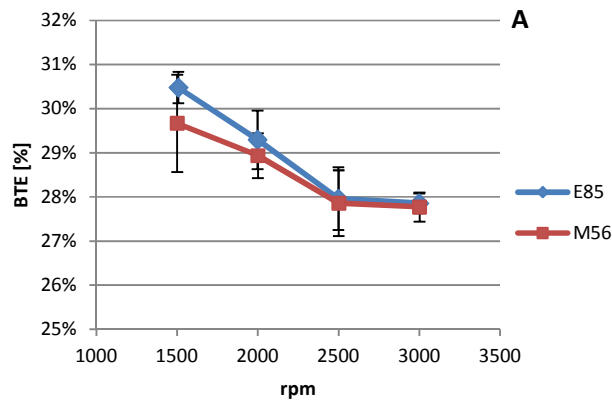


Figure 12 - Brake thermal efficiency as a function of engine speed for different fixed brake torques of 50 Nm (A), 75 Nm (B) and 150 Nm (C).

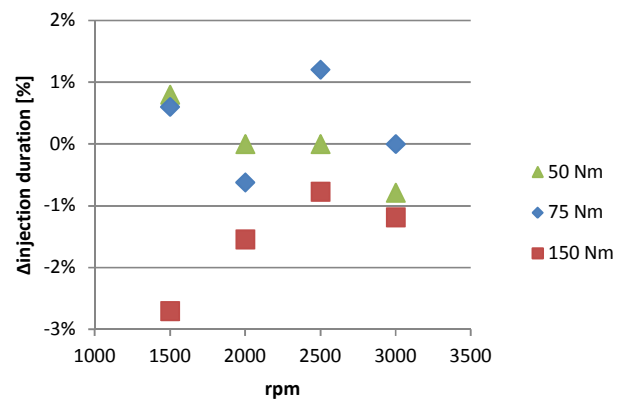


Figure 13 – Difference in injection duration of M56 compared to E85 as a function of engine speed for different fixed brake torques of 50 Nm, 75 Nm and 150 Nm.

As the difference at 150 Nm is the biggest, the combustion characteristics calculated from the in-cylinder pressure data of the AVL IndiModul system were investigated for this load. In Figure 14 and Figure 15, the crank angle at 5% mass fraction burned and the duration of 10-90% mass fraction burned are shown. The main combustion (10-90% mass fraction burned) is similar for both fuels with a slightly slower combustion for M56. The 10-90% mass fraction burned duration increases with $\pm 0.8^\circ\text{ca}$. The biggest difference can be seen for the crank angle at 5% mass fraction burned at 2500 rpm, which could explain the difference in brake thermal efficiency for this operating point. As the fuel-air mixture is never 100% homogeneous in a DI engine, the start of the combustion process could be influenced by small inhomogeneities due to different spray behavior which could lead to different interaction with the incoming air in the combustion chamber.

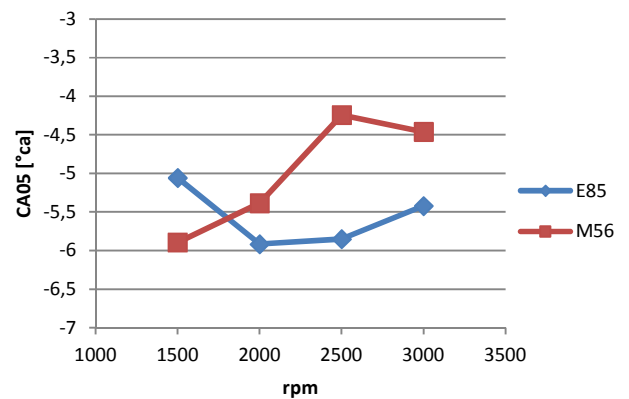


Figure 14 – CA05 as a function of engine speed for a fixed brake torque of 75 Nm.

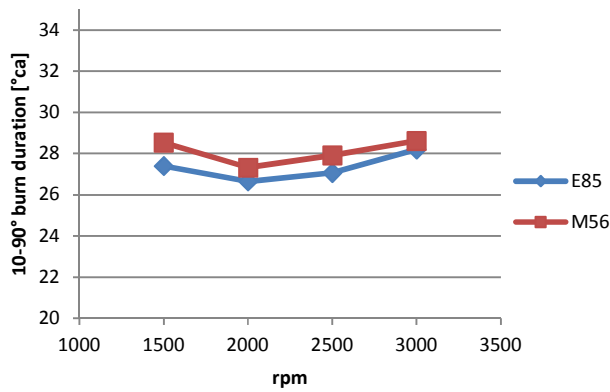


Figure 15 – duration of 10-90% mass fraction burned as a function of engine speed for a fixed brake torque of 75 Nm.

Finally, in Figure 16, Figure 17 and Figure 18, the engine-out NO_x, CO and UHC emissions of E85 and M56 for a fixed torque of 75 Nm are shown as a function of engine speed. There are slightly better engine out emissions for E85 although the error bars overlap for most points and the differences are small compared to M56 for the whole engine speed range. The emissions of both E85 and M56 are close to the emissions of pure ethanol. E85 (85 v/v % ethanol) is close to pure ethanol which explains this behavior.

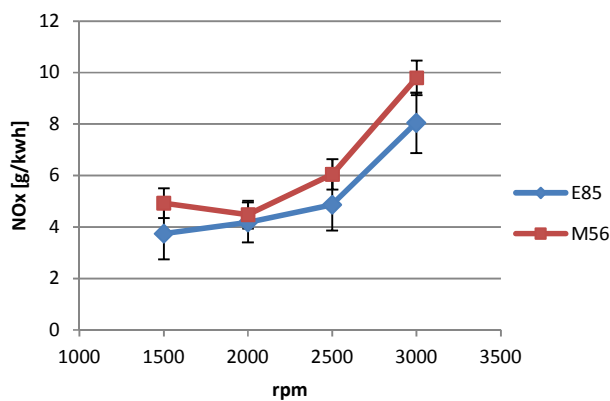


Figure 16 - NO_x emissions as a function of engine speed for a fixed brake torque of 75 Nm.

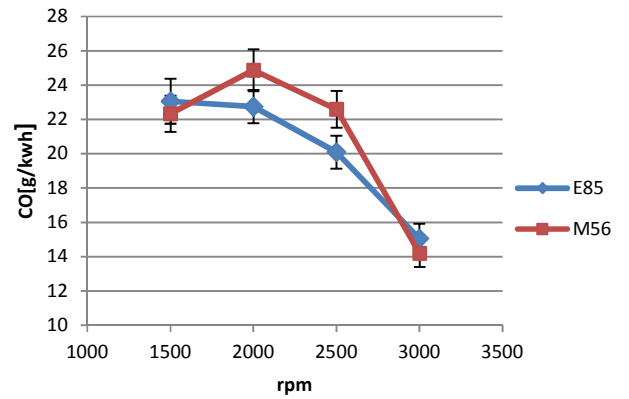


Figure 17 - CO emissions as a function of engine speed for a fixed brake torque of 75 Nm.

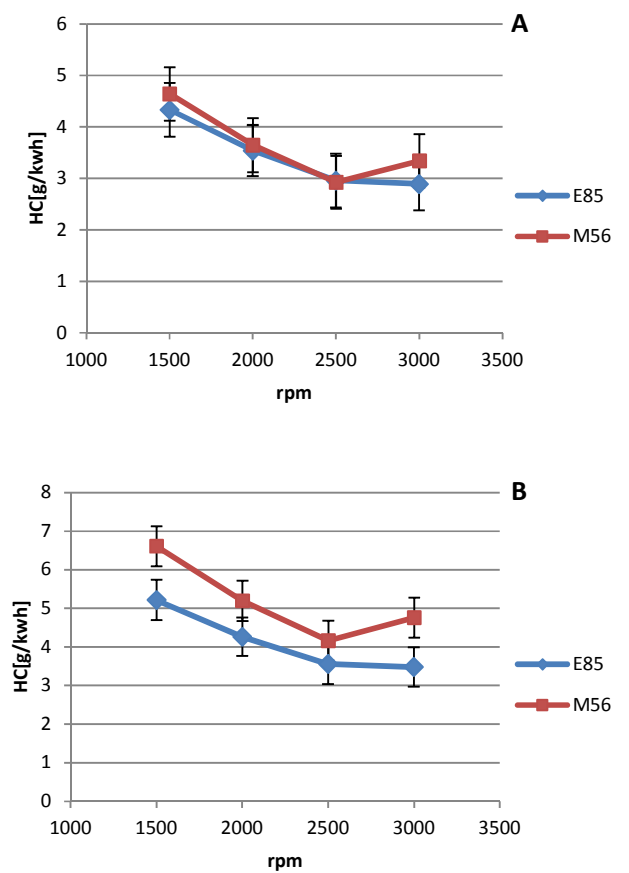


Figure 18 - Uncorrected UHC (A) and corrected UHC emissions (B) as a function of engine speed for a fixed brake torque of 75 Nm

Conclusion

The performance and engine-out emissions (NO_x, CO, HC and PM) of methanol, ethanol and butanol were examined on a 4 cylinder 2.4 DI production engine and are compared with those on neat gasoline. It is shown that the brake thermal efficiency when running on alcohol

fuels is significantly better than with gasoline while emitting fewer emissions. It was clear that methanol was superior both in the case of efficiency and emissions. In a knock limited case for gasoline, the brake thermal efficiency on methanol of almost 40% was more than 5 percentage points better than on gasoline which resulted in a decrease in CO₂ emissions of 20.7 % compared to gasoline.

Additionally, measurements were done for E85 and the iso-stoichiometric methanol-gasoline blend M56 to investigate the hypothesis that iso-stoichiometric blends can be used as drop-in fuels for spark-ignited flex-fuel engines. Special attention was given to the injection duration and the combustion analysis based on the in-cylinder pressure measurements. The engine test results confirmed that, from an engine control point of view, the 'iso-stoichiometric' methanol-gasoline blend can indeed be used as a 'drop-in' fuel for E85. Efficiency and emissions were very similar for both fuels.

Contact Information

Louis Sileghem - Ph. D. fellowship of the Research Foundation Flanders (FWO)

Transport Technology Research Group

Department of Flow, Heat and Combustion Mechanics

Ghent University Sint-Pietersnieuwstraat 41, B-9000 Gent Belgium

louis.sileghem@ugent.be

Acknowledgments

L. Sileghem gratefully acknowledges a Ph. D. fellowship (FWO11/ASP/056) and a grant for a long stay abroad at Argonne National Laboratory provided by the Research Foundation Flanders.

The engine hardware support by Hyundai motor company under Contract No. C1200101, and technical support for engine operation from Dr. Seungmok Choi was also appreciated.

Part of the submitted manuscript has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory ("Argonne"). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

References

[1] Environmental Protection Agency, National Highway Transportation Safety Administration, 2012. 2017 and Later Model Year Light-Duty Vehicle Greenhouse Gas Emissions and Corporate Average Fuel Economy Standards; Final Rule. Federal Register 77, 62623–63200.
[2] The European Parliament and The Council of the European Union. Directive 2009/28/EC of The European Parliament and of The Council of 23 April 2009 on the promotion of the use of energy from Page 12 of 13

renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC. Official Journal of the European Union L 140; 2009.
[3] R.J. Pearson, M.D. Eisaman, J.W.G. Turner, P.P. Edwards, Z. Jiang, V.L. Kuznetsov, K.A. Littau, L. di Marco, S.R.G. Taylor, Energy Storage via Carbon-Neutral Fuels Made From CO₂, Water, and Renewable Energy, Proceedings of the IEEE, 100 (2012) 440-460.
[4] Environmental Protection Agency, "Regulation of Fuels and Fuel Additives: 2012 Renewable Fuel Standards; Final Rule," Federal Register Vol. 77 No. 5, Rev. Jan. 2012
[5] S. Bringezu, H. Schutz, M. O'Brien, L. Kauppi et al., Towards Sustainable Production and Use of Resources: Assessing Biofuels, <http://www.unep.org>, 2009.
[6] T. Wallner, S.A. Miers, S. McConnell, A Comparison of Ethanol and Butanol as Oxygenates Using a Direct-Injection, Spark-Ignition Engine, Journal of Engineering for Gas Turbines and Power-Transactions of the Asme, 131 (2009).
[7] J. Vancoillie, J. Demuynck, L. Sileghem, M. Van De Ginste, S. Verhelst, L. Brabant, L. Van Hoorbeke, The potential of methanol as a fuel for flex-fuel and dedicated spark-ignition engines, Applied Energy, 102 (2013) 140-149.
[8] J. Vancoillie, J. Demuynck, L. Sileghem, M. Van De Ginste, S. Verhelst, Comparison of the renewable transportation fuels, hydrogen and methanol formed from hydrogen, with gasoline – Engine efficiency study, International Journal of Hydrogen Energy, 37 (2012) 9914-9924.
[9] R.J. Pearson, J.W.G. Turner, A.J. Peck, Gasoline-ethanol-methanol tri-fuel vehicle development and its role in expediting sustainable organic fuels for transport, in: IMechE Low Carbon Vehicles Conference, London, UK, 2009, pp. 1-21.
[10] S. Verhelst, Future Vehicles Will Be Driven by Electricity, But Not as You Think, Proceedings of the IEEE, 102 (2014) 1399-1403.
[11] Turner, J.W.G., R.J. Pearson, P. Harrison, et al. "Evolutionary Decarbonization of Transport: a Contiguous Roadmap to Affordable Mobility Using Sustainable Organic Fuels for Transport." IMechE Sustainable Vehicle Technology Conference, Proceedings. 2012.
[12] Turner, J., Pearson, R., Purvis, R., Dekker, E. et al., "GEM Ternary Blends: Removing the Biomass Limit by using Iso-Stoichiometric Mixtures of Gasoline, Ethanol and Methanol," SAE Technical Paper 2011-24-0113, 2011, doi:10.4271/2011-24-0113.
[13] M. Specht, A. Bandi, Renewable carbon-based transportation fuels, Springer Berlin Heidelberg, Berlin, 2006.
[14] M. Specht, F. Staiss, A. Bandi, T. Weimer, Comparison of the renewable transportation fuels, liquid hydrogen and methanol, with gasoline--Energetic and economic aspects, International Journal of Hydrogen Energy, 23 (1998) 387-396.
[15] G.A. Olah, A. Goeppert, G.K. Prakash, Beyond Oil and Gas: the Methanol Economy., Wiley-VCH Verlag GmbH & Co., KGaA, Weinheim, Germany, 2006.
[16] C. Graves, S.D. Ebbesen, M. Mogensen, K.S. Lackner, Sustainable hydrocarbon fuels by recycling CO₂ and H₂O with renewable or nuclear energy, Renewable and Sustainable Energy Reviews, 15 (2011) 1-23.
[17] M. Steinberg, V.D. Dang, Production of synthetic methanol from air and water using controlled thermonuclear reactor power. 1. Technology and energy requirement., Energy Conversion, 17 (1977) 97-112.
[18] A. Bandi, M. Specht, T. Weimer, K. Schaber, CO₂ recycling for hydrogen storage and transportation- electrochemical CO₂ removal and fixation, Energy Conversion and Management, 36 (1995) 899-902.
[19] S. Stucki, A. Schuler, M. Constantinescu, Coupled CO₂ recovery from the atmosphere and water electrolysis – feasibility of a new

- process for hydrogen storage, *International Journal of Hydrogen Energy*, 20 (1995) 653-663.
- [20] Whims, S., 2002, *Pipeline Considerations for Ethanol*, Iowa State University, Ames, IA.
- [21] J.W.G. Turner, R.J. Pearson, E. Dekker, B. Iosefa, K. Johansson, K.A. Bergstrom, Extending the role of alcohols as transport fuels using iso-stoichiometric ternary blends of gasoline, ethanol and methanol, *Applied Energy*, 102 (2013) 72-86.
- [22] L. Sileghem, A. Coppens, B. Casier, J. Vancoillie, S. Verhelst, Performance and emissions of iso-stoichiometric ternary GEM blends on a production SI engine, *Fuel*, 117 (2014) 286-293.
- [23] L. Sileghem, V.A. Alekseev, J. Vancoillie, K.M. Van Geem, E.J.K. Nilsson, S. Verhelst, A.A. Konnov, Laminar burning velocity of gasoline and the gasoline surrogate components iso-octane, n-heptane and toluene, *Fuel*, 112 (2013) 355-365.
- [24] L. Sileghem, V.A. Alekseev, J. Vancoillie, E.J.K. Nilsson, S. Verhelst, A.A. Konnov, Laminar burning velocities of primary reference fuels and simple alcohols, *Fuel*, 115 (2014) 32-40.
- [25] Jung, H., Shelby, M., Newman, C. and Stein, R., "Effect of Ethanol on Part Load Thermal Efficiency and CO₂ Emissions of SI Engines," *SAE Int. J. Engines* 6(1):2013, doi:10.4271/2013-01-1634..
- [26] J.B. Heywood, *Internal Combustion Engine Fundamentals*, MacGraw-Hill, New York, 1988.
- [27] F. Ma, Y. Wang, J. Wang, S. Ding, Y. Wang, S. Zhao, Effects of Combustion Phasing, Combustion Duration, and Their Cyclic Variations on Spark-Ignition (SI) Engine Efficiency, *Energy & Fuels*, 22 (2008) 3022-3028.
- [28] T. Wallner, Correlation Between Speciated Hydrocarbon Emissions and Flame Ionization Detector Response for Gasoline/Alcohol Blends, *Journal of Engineering for Gas Turbines and Power*, 133 (2011) 082801-082801.
- [29] W. Yanju, L. Shenghua, L. Hongsong, Y. Rui, L. Jie, W. Ying, Effects of Methanol/Gasoline Blends on a Spark Ignition Engine Performance and Emissions, *Energy & Fuels*, 22 (2008) 1254-1259.
- [30] D. Turner, H. Xu, R.F. Cracknell, V. Natarajan, X. Chen, Combustion performance of bio-ethanol at various blend ratios in a gasoline direct injection engine, *Fuel*, 90 (2011) 1999-2006.