

Meeting RFS2 Targets with an E10/E15-like Fuel - Experimental and Analytical Assessment of Higher Alcohols in Multi-component Blends with Gasoline

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ABSTRACT

This paper evaluates the potential of adding higher alcohols to gasoline blendstock in an attempt to improve overall fuel performance. The alcohols considered include ethanol, normal- and iso-structures of propanol, butanol and pentanol as well as normal-hexanol (C2-C6). Fuel performance is quantified based on energy content, knock resistance as well as petroleum displacement and promising multi-component blends are systematically identified based on property prediction methods. These promising multi-component blends, as well as their respective reference fuels, are subsequently tested for efficiency and emissions performance utilizing a gasoline direct injection, spark ignition engine. The engine test results confirm that combustion and efficiency of tailored multi-component blends closely match those of the reference fuels. Regulated emissions stemming from combustion of these blends are equal or lower compared to the reference fuels across the tested engine speed and load regime. The presented analytical and experimental results confirm that higher alcohols can be utilized to create fuels with superior properties such as blends that closely mimic the properties of E10/E15 while exceeding the RFS2 fuel blend requirements of approximately 28% ethanol-equivalent alcohol content.

CITATION: Wallner, T., Ickes, A., Lawyer, K., Miers, S. et al., "Meeting RFS2 Targets with an E10/E15-like Fuel - Experimental and Analytical Assessment of Higher Alcohols in Multi-component Blends with Gasoline," *SAE Int. J. Fuels Lubr.* 6(3):2013, doi:10.4271/2013-01-2612.

INTRODUCTION

The U.S. Renewable Fuel Standard has made it a requirement to increase the usage of ethanol and advanced biofuels to 36 (ethanol equivalent) billion gallons by 2022. Conventional ethanol will be capped at 15 billion gallons and the use of at least 1 billion gallons of biomass-based diesel is required, leaving 20 billion gallons to come from other advanced biofuels. Assuming all the advanced biofuel was ethanol, this would result in a renewables fraction of the estimated total amount of finished gasoline consumed in 2022 of approximately 28% (Figure 1).

Currently, renewables are mainly consumed as low level blends in gasoline (E10) as well as a small fraction as E85 in

Flex Fuel Vehicles (FFVs). The U.S. Environmental Protection Agency recently approved the operation of vehicles of model year 2001 and newer on E15 which has an oxygen content of 5.5 wt% [1]. This partial waiver is controversial due to potential vehicle durability issues at elevated blend levels [2]. While this waiver relaxes the limit on ethanol blending in the general gasoline pool (known as the ethanol blend wall) in the short term, the mandated increase of total renewables in finished gasoline is expected to exceed the 15% mark by the middle of this decade.

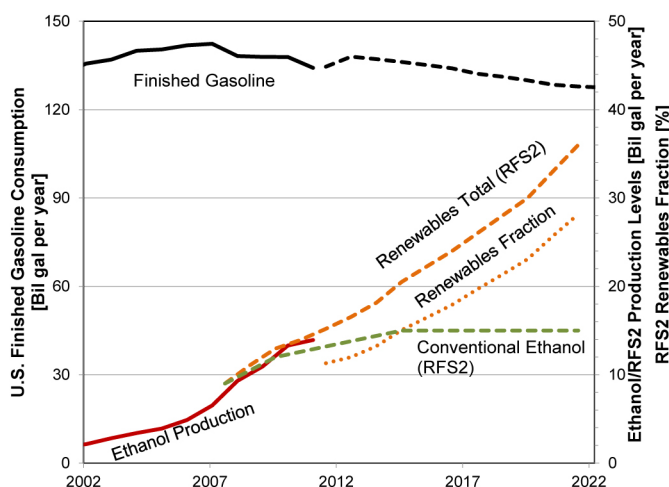


Figure 1. RFS2 targets and estimated renewable fraction [based on 3,4,5]

Due to its high octane number, renewable character and minimal toxicity, ethanol was believed to be one of the most favorable alternative fuels to displace gasoline in spark-ignition engines. However, replacing gasoline with ethanol results in a substantial reduction in vehicle range. Further, higher ethanol blend levels can cause material compatibility issues and require adaptive engine calibrations. Ethanol is fully miscible in water which requires blending at distribution sites instead of the refinery. Higher alcohols, on the other hand, have a higher energy density and lower affinity for water than ethanol, which could mitigate some of the above mentioned issues.

This study is designed to examine whether blends of longer chain alcohols with blendstock for oxygenate blending (BOB) could resemble the relevant fuel characteristics of E10/E15 while improving knock resistance, increasing energy content and/or meeting the RFS2 renewables fraction requirement.

FUEL SPECIFICATIONS

This study was specifically designed to characterize alcohol fuels for gasoline blending including ethanol, normal- and iso-structures of propanol, butanol and pentanol as well as normal-hexanol (C2-C6). Because limited information is available on the engine-relevant properties of a majority of these alcohols, a fuel analysis was performed to provide reliable baseline information for further analysis [6]. Experimental work on a spark ignition engine was also performed prior to this study to identify the combustion and emissions properties of two-components gasoline/alcohol blends at 50 vol% blend level [7]. Prediction methods were developed to calculate the engine-relevant properties of multi-component blends and to allow for an objective comparison with reference fuels [8].

Base Fuel Properties

Fuels used for this study include certification gasoline (EEE) and neat blendstock for oxygenate blending (BOB) as reference fuels as well as BOB mixed with alcohols ranging from ethanol (C2) to hexanol (C6). Table 1 summarizes the relevant properties of the base fuels.

Table 1. Base fuel specifications [6]

	Density kg/m ³	HoV kJ/kg	LHV MJ/kg	Oxygen wt%	RON -	MON -	RVP kPa (psi)
EEE	742	351*	42.9	0	97.1	88.7	62.1 (9.0)
BOB	753	n/a	42.7	0	88.6	81.0	40.0 (5.8)
ethanol	789	920	25.5	34.7	107.4	88.2	17.4 (2.5)
n-propanol	803	792	30.2	26.6	104.9	87.8	8.5 (1.2)
iso-propanol	786	757	29.7	26.6	112.5	96.7	13.3 (1.9)
n-butanol	810	708	32.9	21.6	98.3	84.4	10.1 (1.5)
iso-butanol	802	686	32.7	21.6	105.1	89.3	6.3 (0.9)
n-pentanol	814	647	34.7	18.1	85.8	75.9	3.7 (0.5)
iso-pentanol	810	617	34.5	18.1	98.8	86.8	2.8 (0.4)
n-hexanol	814	486	36.0	15.7	69.3	64.1	2.8 (0.4)

* actual value not available, value shown is typical for gasoline

The density of alcohols is higher than that of EEE and BOB but does not follow a clear trend based on carbon count. Due to the oxygen in the fuel, alcohols have a reduced lower heating value (LHV) compared to gasoline; LHV of the alcohols increases with decreasing oxygen content. The decreased LHV also requires a larger amount of fuel to be introduced to the engine to achieve equivalent delivered energy. Heat of vaporization (HoV) of alcohols is higher than that of gasoline and decreases with increasing carbon count (equivalent to decreasing oxygen content). The increased HoV of alcohols is amplified by the fact that more fuel has to be evaporated due to the reduced LHV. Octane ratings (RON, MON) of alcohols peak at iso-propanol; iso-structures exhibit a higher octane rating than their respective n-structures. Vapor pressure (RVP) of neat alcohols is significantly lower than that of gasoline and decreases with carbon count. A more detailed analysis and comparison of the properties of neat alcohols compared to gasoline can be found in [6].

Blend Property Predictions

Properties of multi-component blends are predicted based on the properties of the neat components. Linear correlations are used to estimate properties such as lower heating value, density and heat of vaporization. An empirical approach is used to predict knock resistance (RON) and vapor pressure (RVP) of multi-component blends. Details on the property prediction methods can be found in [8].

Scenario Definition

Upon completion of the property calculations, promising blends are selected based on specific scenarios. The specific scenario discussed in this study aims at creating multi-component blends with superior properties compared to currently approved E10/E15 blends. Target selection significantly influences the results in terms of blend

composition. A detailed analysis of target value sensitivity can be found in [9].

Table 2. Scenario target criteria and values

Scenario	E10/E15 Alternate
Oxygen content	≤ 5.5 wt% (E15)
LHV	≥ 40.2 MJ/kg (E15)
RON	92.2 (E10)
RVP	38-54 kPa (5.5-7.8 psi)
Petroleum displacement	$\geq$ that of E15
Blendstock	BOB

Table 2 summarizes the scenario target criteria and values applied for this study. These targets include an oxygen content of less than 5.5 wt% which is equivalent to E15 for which a U.S. EPA partial waiver has been granted [1]. In order to avoid a further range penalty with increasing blend levels, a lower heating value target equal to E15 (40.2 MJ/kg) is established. Further targeting utilization in current production vehicles, the RON value of the fuel blend must exceed that of E10 (92.2). Vapor pressure targets are set based on the maximum RVP for ASTM D4814 Class AA gasoline as well as the minimum RVP for ASTM D5798 Class I E85. Finally, it is stipulated that blends meet or exceed E15 in terms of petroleum displacement.

Fuel Selection

Using the properties of BOB and neat alcohols discussed earlier and applying the above mentioned property prediction methods, characteristics of a large range of multi-component alcohol blends are calculated. The targets shown in Table 2 are applied to down-select from the large range of possible combinations of multi-component alcohol blends. Figure 2 graphically shows the results of this down-selection process using energy content and octane rating as examples. Each square represents the properties of a blend; blends that fail to meet the specified RON target (92.2) and/or the LHV target (40.2 MJ/kg) are excluded from consideration. Alcohol fuels with the highest octane rating also have relatively low energy content. This trade-off results in the triangular shape of the remaining blends with increasing energy content along the x-axis and increasing knock resistance on the y-axis. The reference fuels (E10, E15) are also shown in the graph for orientation. The graph further shows the level of petroleum displacement in gray scales based on ethanol equivalent alcohol content.

Despite the range of criteria and target values, a large number of possible combinations still remain once the blends that fail to meet one or multiple criteria have been excluded. Rather than introducing more stringent criteria target values, a selection of 'best-in-class' blends was made. Depending on the specific case, it might be desirable to identify the blend with the highest possible energy content, octane rating or petroleum displacement. These blends are highlighted in Figure 2 and are labeled as 1A(all), 1B(all) and 1C(all), respectively. The graph also shows that a large number of

blends exhibits properties substantially identical to the identified best-in-class blends.

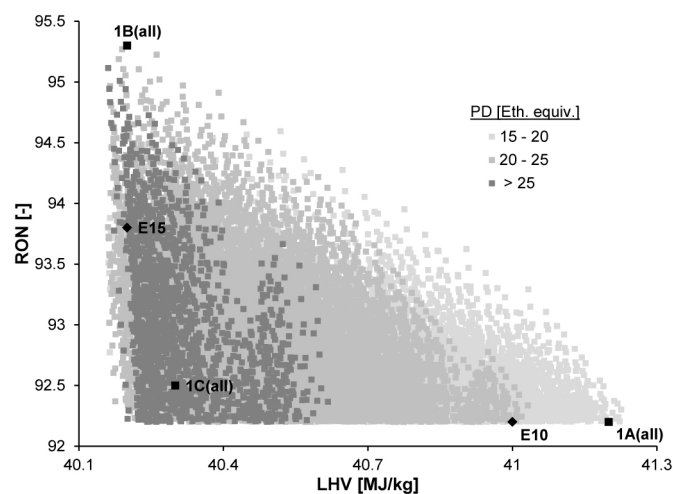


Figure 2. RON and LHV of selected multi-component blends and reference fuels

Due to insufficient information available on large-scale production, cost considerations have so far not been included when assessing the different alcohols. However, recent work in the conversion of ethanol to higher carbon number alcohols suggests that even carbon number alcohols may be more feasible to produce than odd number ones [10]. This specific limitation finds consideration in one fuel blend selected for further analysis that only contains even-number alcohols (in this case C2 and C4). The blend properties of this blend named 1B(even) and the composition and relevant properties of the best-in-class alcohol blends are summarized in Table 3 together with the properties of the reference fuels.

Table 3. Properties of the reference fuels (measured) and tested blends (calculated)

Fuel	eth vol%	i-prop vol%	i-but vol%	i-pent vol%	n-hex vol%	BOB vol%	RON -	LHV MJ/kg	HoV kJ/kg	O2 wt%	PD -
EEE							97.1	42.9	351	0	0
BOB						100	88.6	42.7	351	0	0
E10	10					90	92.2	41.0	407	3.6	10
E15	15					85	93.8	40.2	435	5.5	15
1A(all)		6.5	5	1.5		87	92.2	41.2	398	3.2	16
1B(all)		18	2			80	95.3	40.2	430	5.4	23
1C(all)	2	9		7	4.5	77.5	92.5	40.3	423	5.3	29
1B(even)	12		5			83	93.8	40.2	435	5.5	19

Blend 1A(all), the alcohol blend with the highest energy content exceeds the LHV of the target fuel (E15) by approximately 2.5% at a petroleum displacement equivalent to E16. The blend targeting increased knock resistance, 1B(all), exceeds the E10 reference fuel by 3 points in RON at a petroleum displacement equivalent to E23 while matching E15 in energy content. If only even number carbon alcohols are used to maximize knock resistance, reflected by blend 1B(even), a RON increase of 1.6 points over E10 is

achievable at a petroleum displacement equivalent to E19. 1C(all), the blend targeting the highest petroleum displacement, exceeds E10 in knock resistance and E15 in energy content at a petroleum displacement equivalent to E29, an improvement of 93% over the E15 reference.

ENGINE TEST RESULTS

The engine used for the experimental assessment of the reference fuels and highlighted blends 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 4](#).

Table 4. Engine specifications

Hyundai 2.4L GDI engine	
Model	Theta II
Cylinder count	4
Displacement	2.36 L
Bore	88 mm
Stroke	97 mm
Compression	11.3
Rated power	147 kW at 6300 RPM
Maximum torque	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 a calibration 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 were used. All tests were run with stock, early injection resulting in homogenous charge using a closed loop feedback to tightly control air/fuel ratio to stoichiometric conditions. Fuel trims were adjusted to ensure that stoichiometric operation can be maintained regardless of fuel blend level.

Upon completion of splash blending of the test fuels, a predetermined test sequence was repeated for each of the test fuels. The test sequence included engine warm-up before data was collected. Data sampling was performed at five steady-state engine operating points including 1500 RPM at varying load of 2.62 bar, 4 bar and 8 bar brake mean effective pressure (BMEP) as well as 3000 RPM at 4 bar and 8 bar BMEP. At each load point the engine was allowed to stabilize before two sets of data were taken at a sample frequency of 10 Hz over a period of 120 sec each. For each data set cylinder pressure traces in all four cylinders were also collected for 500 consecutive cycles. Post-processing included determination of the arithmetic average values for the low speed data including standard deviations as well as calculations of cycle-average cylinder pressure and rate of heat release (ROHR) traces.

Combustion Behavior

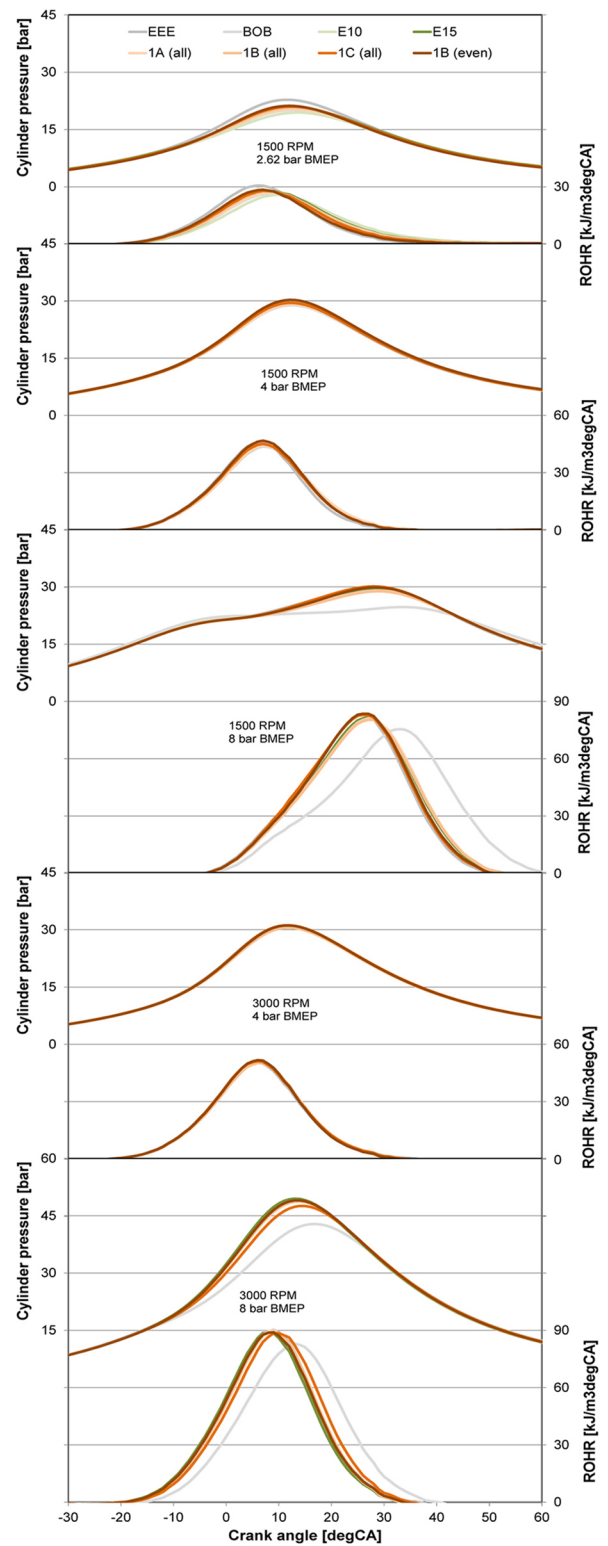


Figure 3. Pressure traces and heat release rates

An overview of the high speed data sets for all operating points is shown in [Figure 3](#) comparing cylinder pressure traces and heat release rates (average of all four cylinders). At