

Options for Use of GTL Naphtha as a Blending Component in Oxygenated Gasoline

Toby Rockstroh and Gareth Floweday
Sasol Advanced Fuels Laboratory, University of Cape Town

Celeste Wilken
Sasol Technology Fuels Technology

ABSTRACT

The benefits of blending ethanol into gasoline fuel are well established. Ethanol's high latent heat of vaporisation and chemical auto-ignition resistance combine in producing significant knock resistance, enabling higher compression ratio and/or higher charge boosting. Its high flame speed characteristics result in shorter burn durations. Its high knock resistance and rapid burning enable ignition phasing optimisation. These factors all improve the efficiency of spark ignition (SI) engines.

Current "flex-fuel" vehicles are designed to operate on both conventional gasoline as well as blends containing higher volumes of ethanol and/or methanol, the former being commonly known as E85. The American Society for Testing and Materials ASTM D5798 specification for ethanol fuel blends was adapted in 2011 to prescribe a minimum ethanol content of 51 % with the remainder able to consist of low octane blending streams. This opens the door for fuel manufacturers to include naphtha streams previously not regarded as suitable for spark ignition engines. In this study Low Temperature Fischer-Tropsch (LTFT) Gas to Liquids (GTL) naphtha, a low octane product of a LTFT GTL refinery, was investigated for suitability of use in oxygenated gasoline fuel blends.

Fuel blends consisting of a mid-grade gasoline, GTL naphtha and ethanol were analysed to compare their octane ratings in relation to gasoline specifications.

The performance of GTL naphtha and ethanol blends (E50 and E85) was compared to petroleum-derived gasoline as well as a High Temperature Fischer-Tropsch (HTFT) Coal to Liquid (CTL) derived synthetic commercial 95 RON gasoline by means of spark advance sweeps conducted on a charge boosted single cylinder Gasoline Direct Injection (GDI) research engine. While the E85 blend exhibited completely knock free operation, it was shown that the E50 blend resulted in similar performance to the commercial gasoline as a consequence of comparable partially knock limited spark advance (KLSA) behaviour.

The study derived blending rules for the simultaneous use of GTL naphtha and ethanol in order to maintain the octane quality of the base gasoline.

CITATION: Rockstroh, T., Floweday, G., and Wilken, C., "Options for Use of GTL Naphtha as a Blending Component in Oxygenated Gasoline," *SAE Int. J. Fuels Lubr.* 9(1):2016, doi:10.4271/2016-01-0879.

INTRODUCTION

The United States (US) Energy Independence and Security Act of 2007 established a Renewable Fuel Standard (RFS2) that prescribes the use of 36 billion gallons of renewable fuels to be used by 2022. Most of the renewable fuel is expected to come from bio-ethanol. [1]. Furthermore it has been suggested that alcohol fuels may potentially have a greater impact in the short term to reduce the effects of climate change due to transportation, rather than electrification of the vehicle fleet or a switch to a hydrogen economy [2] [3]. It has been shown that light alcohols are very good fuels for spark ignition (SI)-engines due to their high octane numbers [4] [5] [6] [7] [8] [9] [10] [11] [12]. In Gasoline Direct Injection (GDI) engines in particular, the high

charge cooling effect of ethanol results in improved knock resistance and cylinder fill rate [9] [10] [11]. Ethanol also offers potential for improved spark timing and reduced adiabatic flame temperature, resulting in a lower exhaust gas temperature which reduces the common need for fuel enrichment under full load conditions to provide thermal protection for certain engine components [7].

Synthetic Low Temperature Fischer Tropsch (LTFT) Gas to Liquids (GTL) fuel refineries produce an ultra-low sulphur diesel distillate product with a high cetane number, thereby making it a very desirable fuel for modern ultra clean diesel engines. GTL naphtha, constituting approximately 20 - 30% of the total refinery yield,

consists predominantly of normal alkanes with virtually no aromatics or sulphur [13]. Sulphur is strictly regulated in most automotive fuel specifications and there is an increasing drive to limit the aromatic content [14]. GTL naphtha has an inherently low octane number thereby making it less valuable as a gasoline blending component. It has therefore been utilised as a high quality ethylene cracker feedstock.

Szybist and West [15] recently investigated the effect of low octane hydrocarbon streams on the knock limit of an E85 oxygenate gasoline fuel and found that significant quantities of n-heptane or low octane straight run gasoline could be included without negatively affecting the octane number or knock resistance. The nonlinear relationship between volumetric ethanol content and octane number has previously been shown by Anderson *et. al.* [16] [17].

In order to evaluate the suitability and efficacy of a fuel component for use in a SI-engine, its burn rate also needs to be considered. Laminar flame speed (LFS) is a fundamental characteristic of a fuel and has been shown to directly influence the combustion behaviour in a SI-engine [18] [19].

This study sought to establish the usefulness of GTL naphtha as a blending component in a gasoline type fuel. The analysis included the evaluation of small quantities in non-oxygenated gasoline as well as low ethanol fraction gasoline (E10), Blendstock for Oxygenate Blending (BOB) and ethanol flex-fuel (E85).

TEST FUELS

GTL Naphtha

The GTL naphtha used in this study was sourced from a commercial plant and analysed according to the requirements for hydrocarbon blend stock as per ASTM D5798-13 (Standard specification for ethanol fuel blends for flexible-fuel automotive spark-ignition Engines. 2013) [20] and ASTM D4814-14b (Standard specification for Automotive Spark-Ignition Engine Fuel. 2014) [21]. All specification requirements of ASTM D5798 were met by the GTL naphtha.

Ethanol

Bio-ethanol meeting the specification requirements of ASTM D4806-11 (Standard specification for denatured fuel ethanol for blending with gasoline for use as automotive spark ignition engine fuel. 2011) [22] was sourced from a South African supplier.

Gasoline

Unleaded gasoline with a Research Octane Number (RON) of 93 (ULG93) was sourced from a local refinery. The sample was analysed according to ASTM D4814 and found to be a suitable proxy for an AKI (Anti Knock Index) 87 fuel used in the context of this study.

For the LFS and engine tests, two RON 95 Commercial Automotive Gasolines (CAGs) were used. One of these fuels was sourced from a HTFT synthetic refinery (SCAG 95) while the other was a conventional petroleum (crude oil) derived gasoline (CCAG 95). A summary of the chemical properties is provided in Table 1 below.

Table 1. Chemical properties of the commercial gasolines tested

Parameter	Units	SCAG 95	CCAG 95	ULG93
Density @15°C	kg/m ³	736.3	746.8	739.0
RON		95.5	95.1	93.2
MON		85.7	85.2	83.6
RVP @ 37.8°C	kPa	64	59	58
Boiling range	°C	30 – 190	31- 194	33 - 208
Paraffins	% Vol	40	50	54
Olefins	% Vol	20	12	14
Aromatics	% Vol	37.9	37.6	31.7
Total ethers	% Vol	2.17*	<0.001	<0.001
Benzene	% Vol	2	2.1	2
Net heat of combustion	MJ/kg	41.8	42.3	42.3

It is noted that the compositional analysis doesn't sum to exactly 100
* The ether content of the SCAG consists predominantly of tert-Amyl methyl ether (TAME)

CHEMICAL PROPERTIES OF GTL NAPHTHA

Two dimensional gas chromatography (GCxGC) analysis of GTL naphtha revealed a predominantly (linear) paraffin make-up with a carbon number distribution ranging predominantly from C5 to C12, but extending to C19. This composition gives GTL naphtha a relatively low density and gasoline like volatility. The predominantly straight chain nature of the paraffins makes it an inherently low octane quality. Although the GCxGC analysis details are proprietary, a detailed chemical analysis is shown in Table 2.

Table 2. Chemical properties of GTL naphtha

Parameter	Units	Value
Density @15°C	kg/m ³	679.3
Initial boiling point (IBP)	°C	38.7
10%, evaporation (v/v)	°C	64
30%, evaporation (v/v)	°C	79.1
50%, evaporation (v/v)	°C	91.8
70%, evaporation (v/v)	°C	104.7
90%, evaporation (v/v)	°C	122.6
Final boiling point (FBP)	°C	171.5
n-Paraffins	Mass %	65.19
Branched paraffins	Mass %	34.21
Cyclic paraffins	Mass %	0.59
Reid vapour pressure @37.8°C	kPa	47.9
Sulphur content	ppm wt	1
Carbon distribution		C5-C19
Net heat of combustion	MJ/kg	43.46

OCTANE NUMBER PREDICTION OF GTL NAPHTHA

The ASTM D2699 [23] and ASTM D2700 [24] test methods are not valid for the respective determination of RON and MON for fuels containing over 25% v/v ethanol or for fuels with octane quality lower than 40. Furthermore, use of the standard Cooperative Fuels Research (CFR) engine to provide an *indication* of octane quality for such high ethanol fraction fuels is challenging, since high oxygenate fraction blends require modifications to the carburettor jets and air intake heating system [25]. An alternative method implemented by Yates *et. al.* [26] was to deviate from the test method and conduct the tests at stoichiometric air-fuel ratio to avoid the limitations imposed by the fixed jet carburation system. Due to the difficulty in determining very low octane numbers with the conventional RON and MON engine tests, the blending octane number (BON) of GTL naphtha was predicted based *in principle* on the American Petroleum Institute (API) Research Project 45 method [27]. This method prescribes that a 20 volume % of a test hydrocarbon is blended with primary reference fuel 60 (PRF60), consisting of 60 volume % iso-octane and 40 volume % n-heptane. The octane rating of PRF60 is 60 by definition, for both RON and MON. According to this methodology the Blending Octane number is then a hypothetical value obtained by extrapolating (linearly) from the rating at 20 volume % test hydrocarbon in the PRF to a predicted rating at 100% concentration of the test hydrocarbon. This value is then indicative of the blend octane value of the test hydrocarbon. However, this blend octane value pertains to its test method base stock and cannot be used to accurately predict octane values in other fuels with alternative base stock chemistry.

Due to GTL naphtha's very low octane properties, a PRF93 fuel was blended with GTL naphtha ranging in concentration from 0 to 30 % as shown in Table 3. From this data the blending RON and MON (BRON and BMON, respectively) were linearly extrapolated as shown in Figure 1 and Figure 2. The BON calculations were performed using both experimental and theoretical octane numbers for the PRF as shown in Table 3 and Table 4 respectively. Notable from the experimental PRF results was the difference between the RON and MON values. Per definition a PRF will have the same RON and MON value which was expected to be 93.0 in this case. The difference between the expected and measured MON value for the PRF (100% PRF93 in Table 3) was attributed to the inaccuracy of the MON engine determination.

Table 3. BON calculation for GTL naphtha in a PRF93 (based on experimental values)

Vol% GTL naphtha	0	5	10	20	30
Vol% PRF93	100	95	90	80	70
RON	93.2	89.8	85.2	77.8	70.8
MON	91.8	88.2	84.6	77.5	70.5
BRON		25.2	13.2	16.2	18.5
BMON		19.8	19.8	20.3	20.8

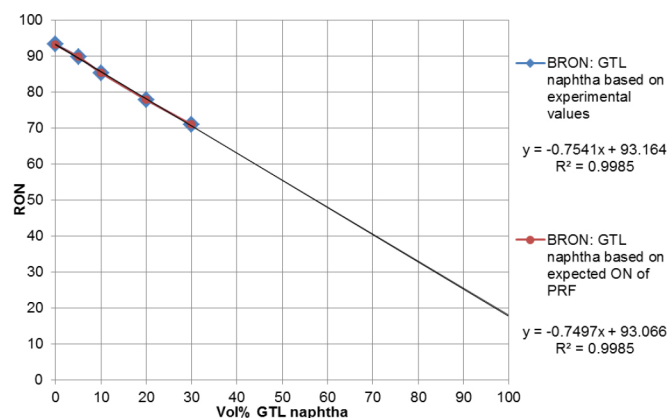


Figure 1. BRON extrapolation of GTL naphtha in PRF93

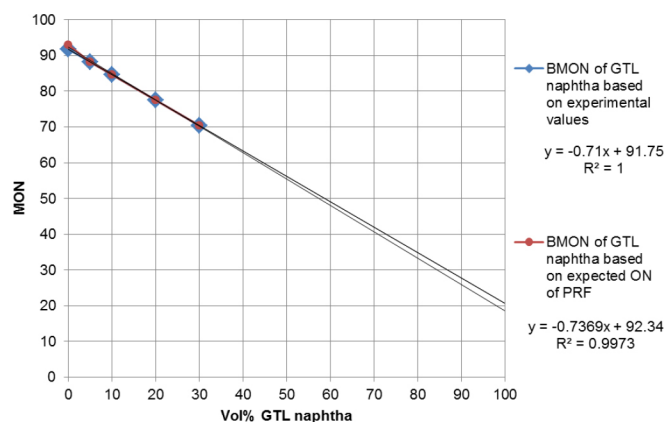


Figure 2. BMON extrapolation of GTL naphtha in PRF93

Table 4. BON calculation for GTL naphtha in a PRF93 (based on theoretical PRF values)

Vol% GTL naphtha	0	5	10	20	30
Vol% PRF93	100	95	90	80	70
RON	93.0	88.3	84	76.4	68.3
MON	93.0	87.7	83.7	76.1	68.2
BRON		-1.0	3.0	10.0	10.7
BMON		-13.0	0.0	8.5	10.3

From Figure 1 and Figure 2 the resulting blending octane number of GTL naphtha with PRF93 was found to be 18.1 RON and 20.7 MON. Figure 3 and Figure 4 show that the BON of GTL naphtha in a market fuel is significantly higher than in the PRF above (Figure 1 & Figure 2). The BONs of GTL naphtha in ULG93 were determined to be 38.1 (BRON) and 46.8 (BMON) respectively. It is noted that negative octane sensitivity (RON minus MON) is not unusual for paraffinic molecules [27]. The contrasting blending octane results associated with the two blending base stocks highlight the limitation of the BON methodology. However, the result using the market fuel was deemed more representative due to octane blend interactions with the wider variety of chemical components making up the market fuel compared to the PRF blend.

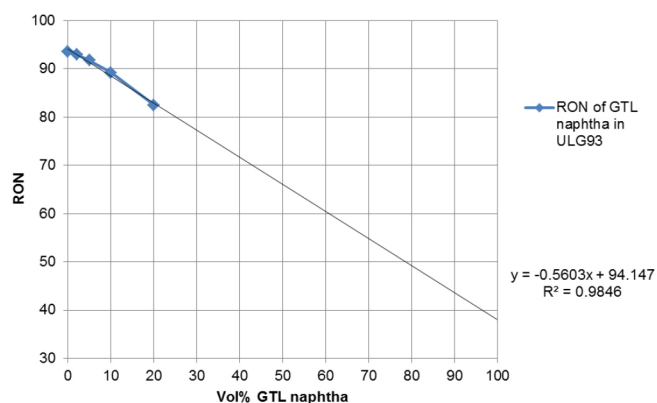


Figure 3. BRON extrapolation of GTL naphtha in ULG93

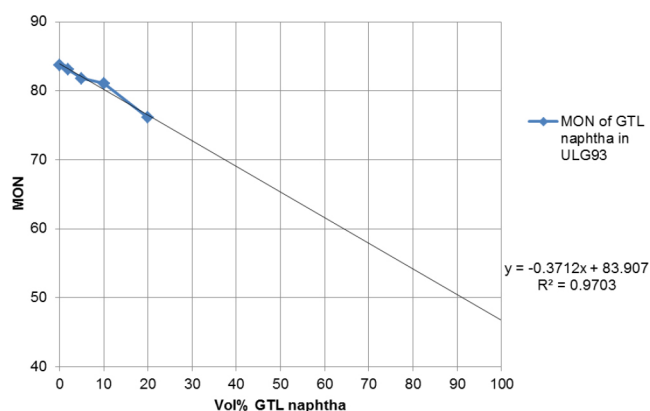


Figure 4. BMON extrapolation of GTL naphtha in ULG93

GTL NAPHTHA AS A GASOLINE BLEND COMPONENT

Gasoline without Oxygenates

In order to evaluate the suitability of GTL naphtha as a gasoline blending component, the two critical performance properties Reid Vapour Pressure (RVP) and AKI were evaluated. For this purpose GTL naphtha was splash blended with a commercial 93 RON unleaded gasoline (termed ULG93), representative of a North American midgrade AKI fuel, up to a concentration of 20% by volume. As shown in Figure 5, the RVP was found to reduce with the addition of GTL naphtha but adhered to the class AA RVP specification of ASTM D4814. The AKI reduced significantly with the addition of GTL naphtha as shown in Figure 6. Only an addition of 2% was possible within the 87 AKI limit for a regular gasoline.

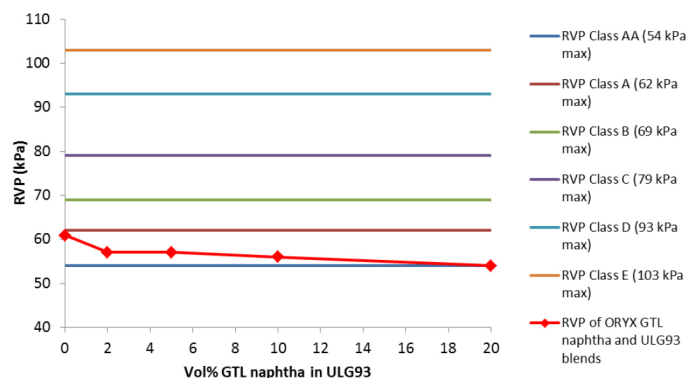


Figure 5. RVP with respect to GTL naphtha content in ULG93

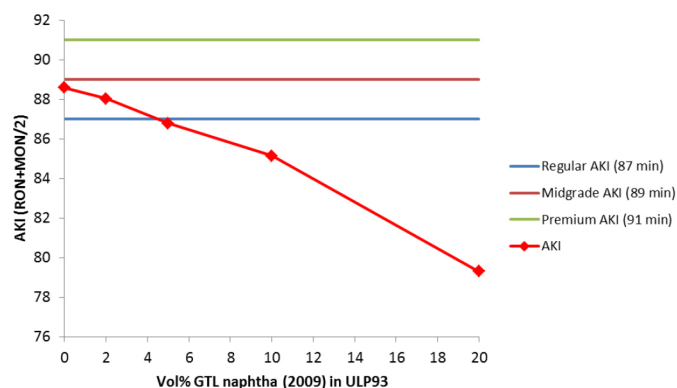


Figure 6. AKI with respect to GTL naphtha content in ULG93

Gasoline with Oxygenates

The current US gasoline specifications allow ethanol content of up to 10% by volume. In 2010 and 2011 the US EPA granted two partial waivers that together allow standard gasoline to contain up to 15% ethanol [28] when supplied to light duty vehicles of model year 2001 and newer, subject to certain conditions [29]. In order to establish the effect of GTL naphtha on the RVP and AKI of ethanol containing gasoline, the 93 RON gasoline fuel was splash blended with ethanol and GTL naphtha in the ratios shown in Table 5.

Table 5. GTL naphtha-ethanol gasoline blends

Blend #	E - blends	Vol% GTL naphtha
E5, N2	E5	2 vol%
E10, N5	E10	5 vol%
E10, N10	E10	10 vol%
E20, N10	E20	10 vol%

The RVP of all the fuel blends was found to be typical of a class A fuel blend as shown in Figure 7. As shown in Figure 8 an E10 gasoline and a 5% GTL naphtha content was found to maintain an AKI of a midgrade gasoline while increasing the GTL naphtha content to 10%, maintained an AKI similar to that of a regular gasoline. Increasing the ethanol content to 20% resulted in the AKI exceeding that of a midgrade gasoline.

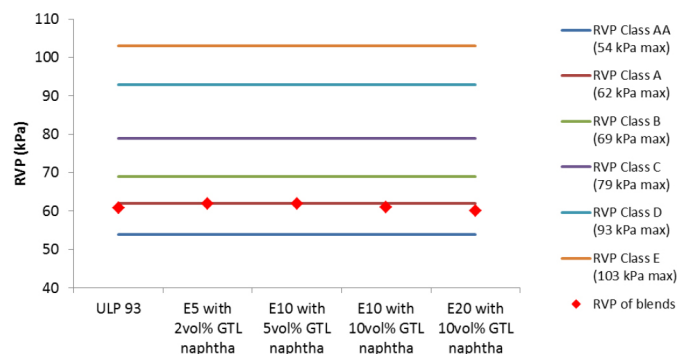


Figure 7. RVP of GTL naphtha-ethanol gasoline blends