THE INFLUENCE OF CHEMICAL COMPOSITION ON IGNITION DELAY TIMES OF GASOLINE FRACTIONS

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To cite this article:

Naser, N., Abdul Jameel, A.G., Emwas, A.H., Singh, E., et al. “[The influence of chemical composition on ignition delay times of gasoline fractions](#)”. Combust. Flame, 209 (2019), pp. 418–429.

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Abstract

Tailoring fuel properties to maximize the efficiency of internal combustion engines is a way towards achieving cleaner combustion systems. In this work, the ignition properties along with the chemical composition (expressed as functional groups) of various light distillate (e.g., gasoline) cuts were analyzed to better understand the properties of full boiling range fuels. Various distillation cuts were obtained with a spinning band distillation system, which were then tested in an ignition quality tester (IQT) to obtain their global chemical reactivity (i.e., ignition delay time (IDT)). The distillates were further analyzed with ¹H nuclear magnetic resonance (NMR) spectroscopy to identify and quantify various functional groups present in them. Various gasolines of research grade with specific target properties set forth by the Coordinating Research Council (CRC) that are known as FACE (fuels for advanced combustion engines) gasolines were distilled. When fuels with low aromatic content were distilled, the higher boiling point (BP) range (i.e., molecular weight) fractions exhibited lower IDT. However, distilled fractions of fuels with high aromatic content showed an initial decrease in IDT with increasing BP, followed by drastic increase in IDT primarily due to increasing aromatic groups. This study provides an understanding on the contribution of various volatile fractions to the IDTs of a multicomponent fuel, which is of relevance to fuel stratification utilized in gasoline compression ignition (GCI) engines to tailor heat release rates.

Keywords: Gasoline; octane sensitivity; autoignition; combustion; ignition delay times; nuclear magnetic resonance

1 INTRODUCTION

One novel approach in achieving global requirements for increased engine efficiency and lower overall greenhouse emissions is co-optimization of fuels and engines. In this regard, designing fuels to match engine requirements and operating conditions becomes imperative. Tailoring chemical and physical properties of fuel to suit each combustion mode in various high efficiency concepts could maximize the internal combustion (IC) engine performance benefits.

A homogeneous charge compression ignition (HCCI) engine, a low temperature combustion (LTC) concept engine, relies mainly on fuel chemistry for its operation. While a partially premixed charge compression ignition (PPCI) engine, utilizes both the thermo-physical properties and chemical properties (autoignition tendency, given by octane number (ON) or cetane number (CN)), to achieve ultra low engine-out emissions as well as high (compression ignition (CI)-like) efficiencies. Similarly, the efficiency of spark ignition (SI) engine depends mostly on the chemical properties (autoignition tendency) of the fuel-air mixture. A fuel exhibiting high resistance to autoignition will allow knock-free operation at high loads, and hence allows higher compression ratio and/or advanced spark timing. In effect, it can be said that an interplay of both the physical and chemical properties of any fuel contributes to the performance of a given engine.

Furthermore, in LTC concepts, such as PPCI, it is desirable to inject a relatively high ON fuel early in the compression stroke. This allows partial premixing of the fuel and air before combustion takes place [1–3]. Such premixing reduces localized high temperature rich zones thereby suppressing soot formation, while the innate low temperature operation results in negligible NO_x formation [3, 4]. Proper implementation of such a concept relies on carefully timing the combustion event over a range of load and speed.

ON is a representative of autoignition of end gas when running an SI engine on a specified fuel. A fuel having higher ON will resist this autoignition. It can also be gauged in terms of ignition delay, the time it takes for a fuel-air mixture to ignite, at a given temperature and pressure condition in the engine combustion chamber. A gasoline mixture is composed of various compounds and hydrocarbon classes, each contributing in varying degree to the net ignition delay time (IDT) of the fuel. Future fuel design will dictate fuel composition tailored to high octane demands of the engine [5, 6]. In this regard, it is necessary to quantify the effect of various hydrocarbon classes on ignition delay of the fuel, and therefore guide refiners for improved fuel quality based on distillation properties. Two sets of ON are used in characterizing a fuel: research octane number (RON) and motor octane number (MON) based on American Society for Testing and Materials (ASTM) standards D2699 and D2700, respectively [7, 8]. The difference between RON and MON is defined as octane sensitivity (OS) ($=\text{RON}-\text{MON}$).

As RON/MON were not able to accurately predict autoignition characteristics in modern engines due to the shift in pressure/temperature history from the standard Cooperative Fuel Research (CFR) engine, new metrics may be desirable. One such metric that has drawn attention recently is the octane index (OI); that takes into consideration of a physical operating condition in addition to the RON/MON of the fuel [9, 10]. OI is defined as a weighted average of RON/MON:

$$OI = (1 - k)RON + kMON \quad (1a)$$

$$OI = RON - k(OS) \quad (1b)$$

Here, the linear weighting factor, k , indicates how far the operating condition is from the RON or MON condition. Many studies have shown that k values in modern SI engines are approaching negative values. Hence, fuels with higher OS would be beneficial in modern SI engines due to higher OI [11–13].

Octane-on-demand (OoD) is another concept that aims to minimize vehicular carbon footprint, by using a high reactivity (low octane) gasoline during normal operation at low to medium loads and a low reactivity (high octane) gasoline fuel at high load knock-prone conditions [14, 15]. However, space and comfort-to-refuelling issues exist when considering dual-fuel concepts in passenger cars [16]. In this regard, on-board separation of a high octane fuel into varying octane components is a viable option [17]. One of the proposed methods of on-board separation depends on distillation of fuel into lighter and heavier components, which may correspond to high reactivity and low reactivity components, respectively. In such an application, the need for analyzing the octane behavior of each distillation cut is critical to the adoption of the technology. In the light of such importance, understanding the ignition behavior of distillation cuts provides a better understanding of the interaction between the physical and chemical properties of a gasoline fuel.

Transportation fuels such as gasolines are composed of several hundred different species [18, 19]. Identification and quantification of such a large number of species are an enormous task. However, these species are in turn composed of a small number of functional groups that mostly determine fuel properties (ON [20], CN [21], sooting propensity [22], etc.). The IDT of a fuel is dependent on its chemical composition (namely, the functional groups) as shown by a number of works [20, 23]. Though the sum total of the functional groups in gasoline is conserved in its distillate fractions, the functional groups in each of the fraction may interact with each other differently (either synergistically or antagonistically) and produce a combined effect that may not correlate linearly with that of the parent fuel. Studies on gasoline fractions enables an understanding of these interactions and their behavior in applications involving gasoline separated into different fractions based on boiling points (BPs) such as OoD. Analyzing these functional groups is a useful way to characterize such complex fuels. ^1H nuclear magnetic resonance (NMR) spectroscopy is a powerful tool that can identify and quantify various functional groups present in

fuels like gasoline [24], diesel [21, 24], base oil [25], and heavy fuel oil [26, 27]. ^1H NMR spectra is represented using chemical shifts (usually between 0-12 ppm) which is the resonant frequency of ^1H nuclei relative to a standard magnetic field. Molecular structure can then be diagnosed from the position and the number of chemical shifts recorded. A significant advantage of ^1H NMR spectroscopy is that different functional groups closely resembling in structure produce distinct signals which makes their analysis easy and quick.

The present work aims to couple a spinning band distillation column with an ignition quality tester (IQT) [28] to estimate the IDTs of separate volume fractions of various non-oxygenated gasolines [29] and two oxygenated certification gasolines. The observations are further correlated with the presence of specific hydrocarbon functional groups, based on NMR spectroscopic data. Hetzel [30] in 1936 investigated the ignition quality of diesel fractions with CN obtained with engine measurements. The diesel used in Hetzel's experiments [30] had a CN of 55 and was separated into 12 equal fractions. Recently, Burger et al. [31] measured the enthalpy of combustion and hydrocarbon family types (using mass spectrometric classification technique) of FACE gasoline fractions. Fuels for advanced combustion engines (FACE) gasolines are research grade fuels with specific target properties viz., RON and OS, such that various laboratories could evaluate fuels with consistent composition and properties set forth by the Coordinating Research Council (CRC) [32]. Classification of hydrocarbon family types in Burger et al. [31] was based on ASTM D2789 standard [31, 33], which characterizes different components in a hydrocarbon mixture into six types. The six types of classification based on ASTM D2789 standard are paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes, indanes and tetralines (grouped together), and naphthalenes. As many of the gasolines in our study contains olefins and classification in this work is based on PIONA (paraffins, *iso*-paraffins, olefins, naphthenes, and aromatics) a direct comparison between our results and the results in Burger et al. [31] was not performed. It was also explicitly stated in [31] that a direct quantitative comparison of the results based on ASTM D2789 method to other classification methods was not always possible. However, the ignition quality of the gasoline fractions were not obtained in their study. To the authors' best knowledge, this is the first work that investigates the ignition quality of gasoline fractions.

This study attempts to use volatility (physical property) and chemical functional groups (chemical property) to better understand fuel autoignition quality (physico-chemical kinetic property). Various boiling ranges can be correlated with the functional groups present in gasolines, which in-turn dictates the autoignition tendency or IDT of the fraction. The data presented could pave a way for future fuel design for better control over desired properties.

2 EXPERIMENTS

In the present study, six FACE and two certification gasolines are fractionated; their important fuel properties are Table 1. Gasolines obtained from fractional distillation of crude oil in general do not contain oxygenates in appreciable amounts. However, oxygenates are added to gasoline feed stock to enhance its ON. The certification gasolines having oxygenates used in the present study are obtained from Coryton Advanced Fuels and Haltermann Solutions, whose properties are obtained from their respective certificates of analysis (COAs).

The gasoline distillates or cuts are obtained with a spinning band distillation system. The distillates obtained were then measured in a King Abdullah University of Science and Technology (KAUST) research-IQT (KR-IQT) at the standard derived cetane number (DCN) condition and at a low temperature condition (ignition delay time sensitivity (IDS) condition explained later) [34]. In addition, spectroscopic analysis of the distillate cuts were obtained with ^1H NMR spectroscopy to quantify the different hydrocarbon classes in each cut. Details on the distillation system, KR-IQT and NMR methodology are explained in the following subsections.

Table 1: Fuel properties

Fuel	FACE A gasoline	FACE C gasoline	FACE F gasoline	FACE G gasoline	FACE I gasoline	FACE J gasoline	Coryton gasoline	Haltermann gasoline
RON	83.5	84.7	94.4	96.8	70.3	71.8	97.5	91.0
MON	83.6	83.6	88.8	85.8	69.6	68.8	86.6	83.4
Sensitivity	-0.1	1.1	5.6	11.0	0.7	3.0	10.9	7.6
Density (kg/m^3)	685	691	707	761	687	741	741	748
AFR _{stoic}	15.18	15.04	14.95	14.55	15.14	14.65	14.47	14.74
H/C ratio	2.29	2.19	2.12	1.84	2.26	1.91	1.78	1.97
Paraffins (v.%)	11.65	24.43	4.40	6.73	14.39	31.64	10.00	13.40
iso-Paraffins (v.%)	85.99	69.73	67.56	38.43	74.54	33.64	38.50	33.70
Olefins (v.%)	0.21	1.27	9.42	8.11	6.35	0.60	10.00	6.80
Naphthenes (v.%)	1.61	0.36	10.98	11.52	3.30	2.29	5.10	15.20
Aromatics (v.%)	0.38	3.92	7.72	33.63	1.15	31.69	32.40	22.70
Oxygenates (v.%)	-	-	-	-	-	-	4.00	8.20

2.1 Spinning band distillation system

The gasoline cuts are obtained with a spinning band distillation system (B/R Instrument Corp., 36-100 high efficiency distillation system), as schematically shown in Fig. S1. The device separates liquids with similar BPs with the use of a helical spinning Teflon band. The vapors of the test fuel generated from the electrically heated round bottom flask condense on externally cooled glass coil. The spinning helical Teflon band creates close contact between the condensing liquid and rising vapor. The spinning band refreshes this dynamic process that results in liquid vapor

equilibration that enables effective separation of liquids with similar BPs. To ensure temperature uniformity of the fluid in the boiling flask, a magnetic stirrer drive was placed beneath the aluminum jacket with a magnetic stirrer in the fluid. The condensates separated are then collected in various receivers as seen in Fig. S1. For each test, 1 L of fuel is placed in the boiling flask and 100 mL of fuel (10% in volume) is collected in each receiver. The device has 8 receivers, thereby 8 cuts and the remaining residue (20% in volume) in the boiling flask provided 9 cuts. More details on the device are available in [35].

The distillation curves of all the gasoline cuts obtained with the spinning band distillation system are shown in Fig. 1 as a function of the vapor temperature.

2.2 KAUST-research ignition quality tester

The KR-IQT is a constant volume combustion chamber pressurized to 21.37 ± 0.1 bar and is heated to a standard temperature prescribed by the ASTM D6890 standard [28]. The results presented below are the average IDT of 32 injections and error bars indicate standard deviation of the readings. More details on the KR-IQT are available in [35, 36].

In addition to IDT measurements at the ASTM D6890 standard [28] condition, IDTs were also measured at a lower temperature, which is referred to the IDS temperature to estimate RON and MON of various gasoline cuts. In recent studies [34, 37], the IDT measured at the standard condition could estimate RON and the IDT measured at the IDS temperature enabled the prediction of OS of the fuel, thus MON.

The RON of various gasoline cuts are predicted with the DCN-RON correlation proposed in [37] as

$$RON = -293 \left(\frac{DCN}{100} \right)^2 - 52 \left(\frac{DCN}{100} \right) + 114.1 \quad (2)$$

The IDS temperature was defined by adjusting the chamber temperature such that an average of 3 *n*-heptane runs provides an IDT of 7.56 ± 0.04 ms (corresponding to twice of the IDT at the standard temperature). The IDS was defined as the ratio between IDTs of non-primary reference fuel (PRF) and PRF at the IDS temperature that have matching DCN at the standard temperature as given in Eq. (3). With the IDT measured at the IDS temperature, the OS can be obtained with Eq. (4). From the predicted RON and OS, MON is estimated as $MON = RON - OS$. More details on the concept of IDS are available in [34, 35].

$$IDS = \frac{IDT_{I,non-PRF}}{IDT_{I,PRF}} \Leftrightarrow DCN_{non-PRF} \approx DCN_{PRF} \quad (3)$$

$$OS = \frac{34 \ln(IDS)}{[0.84 + \ln(IDS)]} \quad (4)$$

Figure 1: Comparison of distillation curves (vapor temperature) for various gasolines obtained with spinning band distillation system.

2.3 Nuclear magnetic resonance (NMR) spectroscopy

NMR spectra were acquired using NMR spectrometer (Bruker 700 MHz AVANACIII) equipped with Bruker CPTCI multinuclear *CryoProbe* (Bruker BioSpin). Details on the sample preparation, signal recording, and assignment of chemical shifts in ^1H NMR measurements are available in the Supplementary Material.

2.4 Determining functional groups

Gasolines are mostly composed of paraffins (*n*- and *iso*-), olefins, naphthenes, aromatics, and oxygenates (usually as added ethanol). The above hydrocarbon classes can be disassembled into the following seven functional groups, namely, paraffinic CH_3 groups, paraffinic CH_2 groups, paraffinic CH groups, olefinic $\text{CH}=\text{CH}_2$ groups, naphthenic $\text{CH}-\text{CH}_2$ groups, aromatic $\text{C}-\text{CH}$ groups, and ethanolic OH groups. Each of these functional groups produces a distinct peak in the ^1H NMR spectra at a characteristic region and an integration allows for a quantification. The ^1H chemical shift assignments used in the present work are reported in Table S1, taken from Abdul Jameel et al. [21]. The ^1H NMR spectra identifies and quantifies only the ^1H nuclei appearing in these functional groups. The quantity of the functional group in the sample are then calculated by adding the contribution of carbon atoms. For example, the relative quantity of paraffinic CH_2 groups (wt%) can be calculated by multiplying the fraction of ^1H nuclei that gives rise to paraffinic CH_2 peaks (from NMR spectra) with the groups molecular weight (i.e., 14) and then dividing the result by the number of ^1H nuclei in the group (i.e., 2). The quaternary aromatic carbons that do not show up in the ^1H NMR spectra are calculated by the knowledge of the hydrocarbon groups in α position to the ring. The procedure and equations to calculate the above functional groups are discussed in detail elsewhere [20, 21].

3 RESULTS AND DISCUSSION

This section details a comparison between the compositional effects on the reactivity of fuels based on ON range. The distillation curves are the manifestation of the compounds, and their functional groups present in the different cuts. The same functional groups affect the reactivity of the cut; hence, all discussions are made from the perspective of functional groups. All the IDT data are plotted with respect to liquid temperature in the boiling flask of the spinning band distillation system. The spacing of the various cuts in the figure indicates the separation in the BP of the respective cuts. The ^1H NMR spectra of full blend gasoline and their respective cuts are available in Figs. S2 to S9.

3.1 High reactivity gasolines

FACE I and J gasolines are characterized as high reactivity gasolines owing to their low ONs (RON of 70.3 and 71.8, respectively) compared to commercial gasolines. Such high reactivity gasolines are potential fuels for PPCI/gasoline compression ignition (GCI) engine applications [38–42]. The distillation curves (liquid temperature) of FACE I and J gasolines obtained with the spinning band distillation system are shown in Figs. 1(a) and 1(b). From the figure, it can be observed that how different compositions given in FACE I and J gasolines influence the BPs of different cuts of gasoline, particularly in the back end (final boiling range). The presence of aromatics in FACE J gasoline (31.7 vol%) causes wider spread in BP due to their larger molecular weights, which is evident from the higher final boiling point (FBP) of FACE J gasoline.

The ignition quality of these various cuts obtained with the spinning band distillation system was measured with the KR-IQT at the standard DCN condition (high temperature) and the IDS condition (low temperature) [34]. Figure 2 shows the IDTs of various cuts of FACE I and J at DCN and IDS conditions along with the various functional groups present in the full blend and each cut. The IDTs of various cuts of FACE I gasoline at the DCN condition in Fig. 2(a) show that cut 1 has the longest IDT due to the higher content of paraffinic CH_3 groups along with the fact that lighter paraffinic hydrocarbons (having lower BPs) having longer IDTs. FACE I gasoline is mostly paraffinic (96.5 wt%) and the quantities of olefinic, naphthenic, and aromatic groups (3.5 wt%) are very small as observed in Fig. 2(e). The ignition quality of such fuels depends on the degree of methyl substitution. The IDT of a paraffinic fuel increases with the increase in the paraffinic CH_3 groups as experimentally demonstrated in a constant volume combustion chamber (CVCC) using the mixtures of C_{16} isomers (*n*-hexadecane, 2,6,10-trimethyltridecane, and 2,2,4,4,6,8,8-heptamethylnonane) [43].

Figure 2: IDT of high reactivity gasolines for FACE I (left panel) and FACE J (right panel) gasolines at (a), (b) DCN and (c), (d) IDS conditions, and functional groups present in various cuts (e), (f).

Abdul Jameel et al. [21] also showed an increase in the IDT of an '*n*-heptane and *iso*-octane' mixture with the increase in the paraffinic CH₃ groups. Methyl substitution also inhibited low temperature chain branching reactions [44]. For heavier cuts (i.e., cuts 2 to 6), the IDT reduces as the paraffinic CH₂ groups increase slowly. For *n*-paraffins and *iso*-paraffins, increasing the chain length (i.e., increasing paraffinic CH₂ groups) results in a higher reactivity thereby shortening the IDT. This trend is observed until cut 6, after which the IDT starts increasing due to heavier components in FACE I gasoline such as aromatics and naphthenes but their fraction is low to cause any significant increase in IDT. The IDT of full blend FACE I gasoline at the DCN condition is 6.78 ms (Fig. 2(a)).

The IDTs of various cuts of FACE J gasoline are shown in Figs. 2(b) and 2(d) at the DCN and IDS conditions, respectively. Note the IDTs for FACE J gasoline are plotted on a logarithmic-scale (as compared with linear-scale for FACE I gasoline), due to a wide spread in their IDTs. Similar to FACE I gasoline, the IDT of cut 1 is slightly longer than cuts (2–6), due to higher methyl substitutions, as seen in Fig. 2(f). The paraffinic CH₃ groups progressively decrease for the cuts 2–6 with increasing chain lengths (paraffinic CH₂ groups). For cuts 8 and 9, very long IDTs are observed because of the existence of large quantities of aromatic C-CH groups present in these cuts. Aromatic C-CH groups have a more prominent effect on the IDT of a fuel compared to other paraffinic, olefinic, and naphthenic groups and tend to increase the IDT significantly [21]. FACE J gasoline has 32.5 wt% of aromatic groups, the largest of all FACE gasolines analyzed here. The IDT of the full blend FACE J gasoline at the DCN condition is 7.39 ms (Fig. 2(b)).

The IDTs of FACE I gasoline cuts at the IDS are observed to decrease with increase in cut number. The IDT of cut 9 at the IDS condition is observed to be even lower than the average, while cut 9 at the DCN condition has higher IDT than the average. However, in general, the trends in the variation of IDT at the IDS condition of various FACE gasoline cuts are observed to be similar to the trends observed at DCN condition with IDT being longer.

3.2 Mid-range octane gasolines

Next, the gasolines with RON/MON in the range of 83.5–84.0, FACE A and C gasoline, are analyzed. The distillation curves of FACE A and C gasolines are similar (Figs. 1(c) and 1(d)). However; their compositions are quite different in terms of, especially, the amount of *n*- and *iso*-paraffins. FACE A gasoline, by design, has a higher composition of *iso*-paraffins indicated by its higher paraffinic CH groups (25.1 wt%), whereas FACE C gasoline contains only 9.5 wt% of paraffinic CH groups. Figure 3 shows the ignition quality of FACE A gasoline cuts, which had fairly similar IDTs in all the cuts; this is because aromatic C-CH groups, with the ability to significantly offset the IDTs of a cut are negligible in FACE A gasoline.

Figure 3: IDT of mid-range octane gasolines for FACE A (left panel) and FACE C (right panel) gasolines at (a), (b) DCN and (c), (d) IDS conditions, and functional groups present in various cuts (e), (f).

Cut 1 of FACE A gasoline has relatively longer IDT than the other cuts, mostly because it has higher paraffinic CH content compared to the other cuts. Generally, the IDT of a mixture increases with an increase in the paraffinic CH groups (branching), as experimentally demonstrated by Abdul Jameel et al. [21] for blends comprising of *n*-heptane, *iso*-octane, 1-hexene, and cyclohexane. This is also seen in the FACE C gasoline cuts, where the paraffinic CH groups increase steadily from cut 1 to 8, while simultaneously increasing the IDT of the cuts. Branching reduces the average chain length and smaller chain paraffins are observed to have longer IDT due to their low reactivities. The cut 9 of FACE C gasoline has lower paraffinic CH groups compared to cut 8, and yet has a higher IDT because of its higher aromatic content. FACE C gasoline has 0.9 wt% of aromatic C-CH groups, most of which shows up in cut 9. The IDTs of cuts 2 to 8 of FACE A gasoline are shorter than FACE C gasoline due to the higher paraffinic CH₂ groups. FACE A gasoline has a higher branching index [21] of 0.42 compared to FACE C gasoline of 0.31.

The IDTs of FACE C gasoline cuts increase monotonically at the DCN condition (Fig. 3(b)). Similar trends are observed at the IDS condition. But differences are observed in the IDTs of FACE A gasoline at the DCN and IDS conditions, where cut 9 is observed to be more reactive at the IDS condition compared to the preceding cut. However, at the DCN condition, cut 9 is less reactive than the preceding cut. Estimations of the RON/MON, as shown later, indicate that cut 9 is observed to have negative OS value. For many reasons this could be attributed to the presence of 3,3,5-trimethylheptane. The BP (= 429 K [45]) of 3,3,5-trimethylheptane corresponds to the boiling range of cut 9 $\approx$ 430 K; the highly branched structure evident from the functional group distribution, and as will be shown later the estimated RON/MON, is close to the nominal RON/MON of 86.5/88.7 obtained from [46].

3.3 High octane gasolines

Because of their high ONs (RON/MON in the range of 85.8–96.8), FACE F and G gasolines are representative of commercial gasolines. It can be observed from Fig. 1(f) that FACE G gasoline had the widest spread in BPs.

Figure 4 shows the ignition quality and the functional group distribution of the full blend FACE F and G gasolines and their cuts. Both fuels have an appreciable distribution of the various functional groups except olefinic CH=CH₂ groups. Cut 1 of FACE F gasoline has longer IDT than cuts 2–8 due to its high paraffinic CH content and low paraffinic CH₂ content. Proceeding from cut 1 to 8, the paraffinic CH groups decrease steadily, whereas the paraffinic CH₂ groups keep on increasing slightly. The quantity of aromatic C-CH groups increases slightly from cut 1 (1.1 wt%) to cut 8 (3.9 wt%) and suddenly increases to 26.8 wt% in cut 9, which is the reason for its high IDT. For FACE gasoline, cut 9 has IDT longer than cut 1 at the DCN

condition. However, at the IDS condition the IDT of cut 9 is shorter than the cut 1. This could be attributed to the higher IDS of aromatics.

The IDT of FACE G gasoline cuts 1–6 at the DCN condition follows a trend similar to FACE F gasoline cuts. However, the cuts 7–9 of FACE gasoline exhibit behavior not observed for other gasolines used in the present study. For cuts 7–9 of FACE G gasoline, the IDTs have large values for cuts 7 and 8 and then the IDT decreases drastically for the cut 9. Note that the IDTs of FACE G gasoline cuts are plotted on a logarithmic-scale. The drastic reduction in IDT for cut 9 of FACE G gasoline could be attributed to the presence of long chain alkanes (isomers of decane and aromatics with C₂-C₄ alkyl substitutions, cf. COA in Supplementary Material), as indicated by the higher paraffinic CH₂ groups in Fig. 4(f).

Figure 4: IDT of high octane gasolines for FACE F (left panel) and FACE G (right panel) gasolines at (a), (b) DCN and (c), (d) IDS conditions, and functional groups present in various cuts (e), (f).

3.4 Oxygenated certification gasolines

The influence of oxygenates (ethanol in this case) in the certification fuels of Coryton and Haltermann gasolines is analyzed. The distillation curves (Figs. 1(g) and 1(h)) show similar trends with a widespread in their BPs. The IDTs and functional groups in Coryton and Haltermann gasolines are shown in Fig. 5. Note that both the IDT scales are logarithmic. Coryton gasoline has a high quantity of aromatic groups (34.7 wt%) along with an appreciable naphthenic CH-CH₂ content (7.6 wt%), whereas Haltermann gasoline has a lower aromatic C-CH content (21.1 wt%) and a higher naphthenic CH-CH₂ content (10.8 wt%). Both fuels contain ethanolic OH groups as observed from the peak in the ¹H NMR spectra between 3.6–3.8 ppm (Figs. S8 and S9). A unit wt% increase in the ethanolic OH groups has a greater impact on fuel ON than any other groups [20], as ethanol acts as a radical scavenger leading to the reduction of fuel reactivity and its low temperature heat release (LTHR) characteristics [47]. Figure 5(a) shows the IDTs of Coryton gasoline and its cuts at the DCN condition. Unlike other gasolines tested here, cut 1 of Coryton gasoline has an appreciable amount of aromatic C-CH groups together with ethanolic OH groups, resulting in relatively short IDT. The IDT increases for cuts 2–7 and for cuts 8 and 9 the IDT are observed be long (note the logarithmic-scale) due to very high aromatic contents 51.7 and 61.0 wt% of aromatics for cuts 8 and 9, respectively.

The Haltermann gasoline cuts are observed to show increasing IDT for the cuts 1–4. However, for the remaining cuts the IDT progressively decreases. The increase in the IDT for cuts 1–4 is mostly due to the increase in the ethanolic OH groups as seen in Fig. 5(f). For the later cuts 5–9, the increase in IDT is not observed even with the increase in aromatic C-CH content. This may be because the later cuts possess a fair quantity of all the different functional groups and the IDT of each cut is due to the net effect of the complex interaction between these individual groups.

The IDTs at the IDS condition are observed to be similar to those at the DCN condition for both Coryton and Haltermann gasolines.

Figure 5: IDT of oxygenated certification gasolines for Coryton (left panel) and Haltermann (right panel) gasolines at (a), (b) DCN and (c), (d) IDS conditions, and functional groups present in various cuts (e), (f).

3.5 *Effects of boiling points on physical delay times*

Numerous research has been published in recent years indicating the importance of fuel's physical properties on combustion, abnormal combustion events such as knock, pre-ignition and superknock, cold-start conditions, emission characteristics, and surrogate fuel formulations [48–57]. Many of the studies indicate the importance of distillation curve characteristics on fuel spray development and fuel stratification in direct injection (DI) engines.

As the IQT uses a liquid fuel injection system, the total IDT is a combination of physical and chemical delay times [35, 58]. The physical delay times (PDTs) of various gasoline cuts were obtained with a point of inflection (POI) approach that is based on the change of curvature of the IQT pressure trace that occurs after the start of injection (SoInj); more details on the approach is described in [59]. The relative contribution of the PDTs to the total IDTs of each gasoline cut at both conditions (DCN and IDS) is shown in Fig. 6. For all the fuels studied in this work, the relative contribution of the PDTs to the IDT was less than 50%. The largest contribution of PDT was observed for FACE J gasoline cut 6, which has also the lowest predicted ONs as shown in the next subsection. The PDTs of all fuels are more or less consistent with marginal increase for heavier cuts, but all PDTs were less than 2.6 ms as shown in Fig. S10. However, depending on the total IDT including the chemical delay times, their contribution varies for each cut.

For each gasoline, the influence of BPs on the PDT contribution to IDT is minimal and reflective of an inverse variation of the IDT. For high reactivity gasolines with low aromatic content, the importance of PDTs increases steadily due to the increasing PDTs and reducing IDTs for heavier cuts (cf. Figs. 2 and S10). The light cuts of these gasolines containing appreciable amount of aromatics have appreciable physical process contribution, but heavier cuts are predominantly influenced by the chemical processes as observed in Fig. 6 (b). Similar observations can be made for mid-range octane gasolines, for gasolines with considerable amount of aromatics the relative contribution of physical processes reduce for heavier cuts containing aromatics. With increasing ONs, i.e., for high octane gasolines and oxygenated certification gasolines, the influence of physical processes on ignition also reduces. This could be attributed to the consistent PDTs for different gasolines and their cuts and increasing IDTs for increasing ONs.

Figure 6: Comparison of the relative contribution of the PDTs of various fractional cuts in terms of T_{liquid} (liquid temperature in the boiling flask).

3.6 Prediction of RON and MON of gasoline fractional distillates

As the IDTs are obtained based on the ASTM D6890 standard condition and the low temperature IDS condition, the RON and MON are estimated with the correlations obtained in [34, 37] (correlations with uncertainties obtained from [35]). The RON of various gasoline fractional distillates are estimated with the DCN using Eq. (5). The IDT measurements at the IDS condition are used in determining the IDS with Eq. (3), from which OS is estimated with Eq. (6), and then MON, more details on IDS and prediction of OS from IDS are available in [34, 35]. The estimated RON and MON of the fractional cuts of various FACE and certification gasolines are shown in Fig. 7, which are plotted against the liquid fuel temperature (T_{liquid}) in the boiling flask. The nominal RON and MON of the full blend gasolines obtained from COAs are also shown.

$$RON_{predicted} = (-293 \pm 10) \left(\frac{DCN}{100} \right)^2 + (-52 \pm 6) \left(\frac{DCN}{100} \right) + (114.1 \pm 1) \quad (5)$$

$$OS_{predicted} = \frac{(34 \pm 2) \ln(IDS)}{[(0.84 \pm 0.2) + \ln(IDS)]} \quad (6)$$

The results show that for most of the fuel fractional cuts, the RON is higher than its MON, i.e., they have positive OS. However, some fractional cuts are observed to have negative OS. Cut 9 of FACE F gasoline has estimated OS of -3.7 , which could be attributed to the presence of branched isomers of heptane and octane (cf. detailed hydrocarbon analysis report (DHA) of FACE F gasoline in Supplementary Material) such as 2-methylhexane, 3-methylhexane, and 2,3-dimethylhexane that are shown to exhibit negative OS [60]. It can also be observed that a greater spread in ON is observed for fuels containing more aromatic content. It is interesting to note that some of the cuts of FACE J gasoline have very low ONs, cut 6 has RON and MON near zero values.

The predicted RON and MON of the fractional cuts could provide guidelines on the design of future fuels depending on engine application. For example, it may not be advisable to use a gasoline such as FACE F gasoline for OoD engine application by on-board separation, as this would result in a high reactive high OS fuel and high octane, low or negative OS fuel. The operation of such a high octane, low or negative OS fuel at higher load condition would result in a fuel with lower OI where a fuel with higher OI would be required [11, 61].

Figure 7: Comparison of estimated RON and MON of various gasoline fractional distillates in terms of T_{liquid} (liquid temperature in the boiling flask) along with full blend RON and MON from COAs.

4 CONCLUDING REMARKS

A spinning band distillation system was utilized in separating different fractional cuts of FACE and certification gasolines. The ignition qualities of various cuts were then analyzed with the KR-IQT at two different temperature conditions to assess the effect of chemical composition of different fractions on their IDTs. The cuts were also analyzed with high resolution ^1H NMR spectroscopy to identify and quantify seven different functional groups. The influence of these functional groups on the IDT of each cut was analyzed.

For fuels with low-ON low-OS (FACE I gasoline), the IDTs at both high and low temperature conditions decreases continuously with the increase in T_{liquid} . This is expected because such fuels have low aromatic content and high paraffinic CH_2 groups (longer chains) in the last cuts which are also observed to have high reactivity. For fuels with low-ON mid-OS (FACE J gasoline), the IDT is observed to decrease slightly up to their middle cuts, but the later cuts have large IDTs compared to initial cuts. This is due to the presence of higher aromatic content that have high-OS and low reactivity. For fuels with mid-ON low-OS (FACE A gasoline), the IDTs are observed to be comparable with negligible spread in IDTs. While a greater spread in IDTs was observed for mid-ON mid-OS (FACE C gasoline). The IDTs of high-ON mid-OS (FACE F gasoline) are observed to have considerable spread in IDTs at the high and low temperature conditions. The greatest spread in IDTs was observed for high-ON high-OS (FACE G gasoline). For oxygenated certification gasolines, the effect of ethanol on the reactivity of the distillate cuts was evident. The effects of BPs on physical and chemical delay times were analyzed. A consistent PDT for different cuts of different gasoline results in chemical delay times being the major contributor to the total IDT, which are dictated by the constituents in each cut of gasoline. The RON and MON of various gasoline fractional cuts was also estimated; that could provide guidelines on the selection of components for fuel design.

ACKNOWLEDGMENTS

This study was funded by Saudi Aramco and the Clean Combustion Research Center at King Abdullah University of Science and Technology (KAUST) under the FUELCOM program. The authors also acknowledge funding from the KAUST Clean Fuels Consortium and its members.

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SUPPLEMENTARY MATERIAL: THE INFLUENCE OF CHEMICAL COMPOSITION ON IGNITION DELAY TIMES OF GASOLINE FRACTIONS

S1 SPINNING BAND DISTILLATION SYSTEM

Figure S1: Schematic of spinning band distillation system. Reproduced with permission from B/R instruments.

S2 NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

The NMR spectra were acquired using NMR spectrometer (Bruker 700 MHz AVANACIII) equipped with Bruker CPTCI multinuclear *CryoProbe* (Bruker BioSpin). Samples were prepared by dissolving 70 μL of a sample (various gasolines and their cuts) in 600 μL of deuterated chloroform CDCl_3 solvent inside 5 mm NMR tubes. To

achieve a high signal-to-noise ratio, the ^1H NMR spectra were recorded by collecting 64 scans with a recycle delay time of 10 s. Each spectrum was recorded using one-pulse sequence through a standard (zg) program from a pulse library (Bruker). The temperature for all experiments was maintained at 298 K. Chemical shifts were determined relative to a solvent peak for CDCl_3 at 7.24 ppm as an internal chemical shift reference. The flame ionization detector (FID) signals were amplified by applying exponential line-broadening factor of 0.3 Hz prior to a Fourier transformation. Software (Bruker BioSpin, Topspin 3.5pl7 and MesReNova) were used to collect and analyze the data.

Table S1: ^1H NMR assignments.

Chemical shift [ppm]	^1H type
6.42–8.99	Aromatic CH groups
4.50–6.42	Olefinic CH and CH_2 groups
3.60–3.80	Ethanolic OH groups
2.88–3.40	CH group α to aromatic ring
2.64–2.88	CH_2 group α to aromatic ring
2.04–2.64	CH_3 group α to aromatic ring
1.57–1.96	Naphthenic CH and CH_2 groups
1.39–1.57	Paraffinic CH groups
0.94–1.39	Paraffinic CH_2 groups
0.25–0.94	Paraffinic CH_3 groups

Figure S2: ^1H NMR spectra of FACE I gasoline and their cuts.

Figure S3: ^1H NMR spectra of FACE J gasoline and their cuts.

Figure S4: ^1H NMR spectra of FACE A gasoline and their cuts.

Figure S5: ^1H NMR spectra of FACE C gasoline and their cuts.

Figure S6: ^1H NMR spectra of FACE F gasoline and their cuts.

Figure S7: ^1H NMR spectra of FACE G gasoline and their cuts.

Figure S8: ^1H NMR spectra of Coryton gasoline and their cuts.

Figure S9: ^1H NMR spectra of Haltermann gasoline and their cuts.

Figure S10: Comparison of the relative contribution of the physical delay times of various fractional cuts in terms of T_{liquid} (liquid temperature in the boiling flask)

DETAILED HYDROCARBON ANALYSIS (DHA) REPORT OF FACE F GASOLINE

Hydrocarbon Expert V4.2

Sun Jun 16 13:26:28 2013

Page 1

File: C:\PIONA3\13-00769_FID2_B.CDF
Sample: KAUST SAMPLE # F
Parameter: C:\HPCHEM\HCE4\13-00769_KAUST#F
LIMS Id:

3/24/2013 1:21:54 PM
Operator: AMA

Summary by Group

<u>Group</u>	<u>%Wgt</u>	<u>%Vol</u>	<u>%Mol</u>
Paraffin	3.796	4.228	4.775
I-Paraffins	65.515	67.355	60.966
Aromatics	9.450	7.661	8.405
<i>Mono-Aromatics</i>	9.450	7.661	8.405
<i>Naphthalenes</i>	0.000	0.000	0.000
<i>Naphtheno/Olefino-Benz</i>	0.000	0.000	0.000
<i>Indenes</i>	0.000	0.000	0.000
Naphthenes	12.191	11.473	15.799
<i>Mono-Naphthenes</i>	12.191	11.473	15.799
<i>Di/Bicyclo-Naphthenes</i>	0.000	0.000	0.000
Olefins	9.026	9.264	10.036
<i>n-Olefins</i>	0.242	0.249	0.181
<i>Iso-Olefins</i>	8.769	9.000	9.838
<i>Naphtheno-Olefins</i>	0.000	0.000	0.000
<i>Di-Olefins</i>	0.015	0.015	0.017
Oxygenates	0.000	0.000	0.000
Unidentified	0.023	0.018	0.020
Plus	0.000	0.000	0.000

Recovery = 100.00

DETAILED HYDROCARBON ANALYSIS (DHA) REPORT OF FACE F GASOLINE

Hydrocarbon Expert V4.2

Sun Jun 16 13:26:28 2013

Page 1

File: C:\PIONA3\13-00769_FID2_B.CDF
Sample: KAUST SAMPLE # F
Parameter: C:\HPCHEM\HCE4\13-00769_KAUST#F
LIMS Id:

3/24/2013 1:21:54 PM
Operator: AMA

Components by Group

Group	Time	Component	%Wgt	%Vol	%Mol
Paraffin	8.171	n-Butane	1.713	2.082	2.792
	10.205	n-Pentane	0.041	0.046	0.054
	15.138	n-Hexane	0.012	0.013	0.014
	25.109	n-Heptane	2.018	2.076	1.907
	81.288	n-Decane	0.011	0.011	0.007
I-Paraffins	7.811	i-Butane	0.037	0.047	0.060
	8.353	2,2-Dimethylpropane	0.007	0.008	0.009
	9.489	i-Pentane	7.369	8.366	9.674
	11.552	2,2-Dimethylbutane	4.218	4.571	4.636
	13.067	2,3-Dimethylbutane	1.205	1.281	1.325
	13.290	2-Methylpentane	0.414	0.446	0.455
	14.096	3-Methylpentane	0.188	0.199	0.207
	16.899	2,2-Dimethylpentane	0.008	0.008	0.008
	17.387	2,4-Dimethylpentane	3.460	3.618	3.271
	17.858	2,2,3-Trimethylbutane	0.036	0.037	0.034
	19.674	3,3-Dimethylpentane	0.137	0.139	0.130
	20.981	2-Methylhexane	1.795	1.860	1.696
	21.181	2,3-Dimethylpentane	5.280	5.343	4.991
	21.964	3-Methylhexane	2.275	2.329	2.151
	23.217	3-Ethylpentane	0.213	0.215	0.202
	23.682	2,2,4-Trimethylpentane	20.950	21.300	17.373
	30.186	2,5-Dimethylhexane	1.646	1.670	1.365
	30.339	2,2,3-Trimethylpentane	0.564	0.554	0.467
	30.502	2,4-Dimethylhexane	2.141	2.150	1.775
	33.143	2,3,4-Trimethylpentane	5.760	5.636	4.777
	33.835	2,3,3-Trimethylpentane	4.934	4.779	4.091
	35.052	2,3-Dimethylhexane	1.566	1.547	1.299
	35.266	2-Methyl-3-ethylpentane	0.061	0.061	0.051
	36.151	2-Methylheptane	0.063	0.064	0.052
	36.411	4-Methylheptane	0.021	0.021	0.017
	36.577	3-Methyl-3-ethylpentane	0.135	0.134	0.112
	36.679	3,4-Dimethylhexane	0.160	0.157	0.133
	37.484	3-Methylheptane	0.059	0.059	0.049
	45.491	2,3,4-Trimethylhexane	0.128	0.122	0.095
	48.559	2,2,3-Trimethylhexane	0.024	0.024	0.018
	50.040	2,5-Dimethylheptane	0.068	0.066	0.050
	55.161	2,3-Dimethylheptane	0.035	0.034	0.026
	61.140	C10 - IsoParaffin - 1	0.030	0.029	0.020
	61.343	C10 - Isoparaffin - 2	0.184	0.177	0.122
	65.358	3,3,5-Trimethylheptane	0.131	0.127	0.087
	68.792	2,3,6-trimethylheptane	0.070	0.049	0.047
	70.437	2,5-Dimethyloctane	0.019	0.018	0.013
	71.129	C10 - IsoParaffin - 3	0.037	0.036	0.025
	77.880	Heptane, 2,2,3,5-tetramethyl-	0.032	0.023	0.020
	79.050	C10 - IsoParaffin - 7	0.018	0.018	0.012
	84.346	C11 Isoparaffin - 4	0.023	0.021	0.014

Recovery = 100.00

DETAILED HYDROCARBON ANALYSIS (DHA) REPORT OF FACE F GASOLINE

Hydrocarbon Expert V4.2

Sun Jun 16 13:26:28 2013

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File: C:\PIONA3\13-00769_FID2_B.CDF
Sample: KAUST SAMPLE # F
Parameter: C:\HPCHEM\HCE4\13-00769_KAUST#F
LIMS Id:

3/24/2013 1:21:54 PM
Operator: AMA

Components by Group

Group	Time	Component	%Wgt	%Vol	%Mol
I-Paraffins	85.515	C11 IsoParaffin - 6	0.012	0.012	0.007
Aromatics					
Mono-Aromatics	52.348	Ethylbenzene	1.352	1.097	1.206
	54.603	m-Xylene	4.123	3.356	3.679
	54.874	p-Xylene	1.730	1.414	1.544
	60.355	o-Xylene	1.988	1.589	1.774
	67.406	i-Propylbenzene	0.017	0.014	0.013
	76.161	1-Methyl-2-ethylbenzene	0.210	0.168	0.166
	78.383	1,2,4-Trimethylbenzene	0.030	0.024	0.023
Naphthalenes					
Naphtheno/Olefins					
Indenes					
Naphthenes					
Mono-Naphthene	12.990	Cyclopentane	10.777	10.171	14.556
	21.501	1,1-Dimethylcyclopentane	0.042	0.039	0.041
	22.738	1t,3-Dimethylcyclopentane	0.087	0.082	0.084
	23.082	1c,3-Dimethylcyclopentane	0.092	0.087	0.088
	23.427	1t,2-Dimethylcyclopentane	0.112	0.105	0.108
	27.958	1c,2-Dimethylcyclopentane	0.027	0.026	0.026
	28.088	Methylcyclohexane	0.059	0.054	0.057
	29.965	Ethylcyclopentane	0.017	0.016	0.017
	39.445	3c-Ethylmethylcyclopentane	0.871	0.799	0.735
	40.631	1,1-Methylethylcyclopentane	0.015	0.014	0.013
	43.602	C8 - MonoNaph - 3	0.038	0.034	0.032
	47.111	Cycloheptane, methyl-	0.036	0.032	0.031
	80.139	1t-Methyl-2-n-propylcyclohexan	0.018	0.016	0.012
Di/Bicyclo-Naphth					
Olefins					
n-Olefins	62.809	Nonene-1	0.242	0.249	0.181
Iso-Olefins	14.430	2-Methylpentene-1	8.655	8.891	9.742
	15.071	2-Ethylbutene-1	0.019	0.019	0.022
	16.566	3-methyl-c-pentene-2	0.012	0.012	0.014
	25.399	2-Methyl-2-hexene	0.017	0.016	0.016
	69.077	2-Methyl-3-ethyl-2-heptene	0.018	0.018	0.012
	77.880	3-Ethyl-2-methylheptene-2	0.032	0.032	0.021
	78.947	C10-iso-olefin-9	0.016	0.011	0.010
Naphtheno-Olefins					
Di-Olefins	15.845	2-methyl-1,4-pentadiene	0.015	0.015	0.017
Oxygenates					
Unidentified	60.078	Unidentified	0.023	0.018	0.020
Plus					

Recovery = 100.00

DETAILED HYDROCARBON ANALYSIS (DHA) REPORT OF FACE G GASOLINE

Hydrocarbon Expert V4.2	Thu Apr 02 11:21:35 2015	Page 1
File: C:\PIONA3\FT-0136A_FID2_B.CDF Sample: FT-00136A Parameter: C:\HPCHEM\HCE4\G95-OLEFIN_2015FID2_B LIMS Id:		2/22/2015 3:23:31 PM Operator: imran

Summary by Group

<u>Group</u>	<u>%Wgt</u>	<u>%Vol</u>	<u>%Mol</u>
Paraffin	5.749	6.891	7.779
I-Paraffins	39.636	43.504	38.167
Aromatics	37.541	32.017	31.694
<i>Mono-Aromatics</i>	36.408	31.136	30.933
<i>Naphthalenes</i>	0.000	0.000	0.000
<i>Naphtheno/Olefino-Benz</i>	0.000	0.000	0.000
<i>Indenes</i>	1.133	0.881	0.761
Naphthenes	10.780	10.696	14.006
<i>Mono-Naphthenes</i>	10.780	10.696	14.006
<i>Di/Bicyclo-Naphthenes</i>	0.000	0.000	0.000
Olefins	6.036	6.646	7.799
<i>n-Olefins</i>	2.293	2.596	3.008
<i>Iso-Olefins</i>	3.165	3.490	4.058
<i>Naphtheno-Olefins</i>	0.578	0.560	0.732
<i>Di-Olefins</i>	0.000	0.000	0.000
Oxygenates	0.259	0.246	0.556
Unidentified	0.000	0.000	0.000
Plus	0.000	0.000	0.000

Recovery = 100.00

DETAILED HYDROCARBON ANALYSIS (DHA) REPORT OF FACE G GASOLINE

Hydrocarbon Expert V4.2

Thu Apr 02 11:21:35 2015

Page 1

File: C:\PIONA3\FT-0136A_FID2_B.CDF
Sample: FT-00136A
Parameter: C:\HPCHEM\HCE4\G95-OLEFIN_2015FID2_B
LIMS Id:

2/22/2015 3:23:31 PM
Operator: imran

Summary by Carbon

C#	%Wgt	%Vol	%Mol
C2	0.259	0.246	0.556
C4	2.853	3.699	4.858
C5	16.589	18.310	23.183
C6	9.934	10.914	11.574
C7	14.278	14.492	14.554
C8	19.446	19.679	17.178
C9	21.238	18.339	17.452
C10	10.635	10.371	7.549
C11	3.298	2.784	2.202
C12	1.471	1.167	0.895

Recovery = 100.00

DETAILED HYDROCARBON ANALYSIS (DHA) REPORT OF FACE G GASOLINE

Hydrocarbon Expert V4.2	Thu Apr 02 11:21:35 2015	Page 1
File: C:\PIONA3\FT-0136A_FID2_B.CDF Sample: FT-00136A Parameter: C:\HPCHEM\HCE4\G95-OLEFIN_2015FID2_B LIMS Id:		2/22/2015 3:23:31 PM Operator: imran

Composite by Carbon

Group	C#	%Wgt	%Vol	%Mol
Paraffin	C4	2.793	3.618	4.756
	C5	0.573	0.686	0.786
	C6	0.398	0.453	0.457
	C7	1.100	1.207	1.087
	C8	0.473	0.505	0.410
	C9	0.230	0.241	0.178
	C12	0.182	0.181	0.106
I-Paraffins	C4	0.060	0.081	0.102
	C5	5.338	6.461	7.323
	C6	5.546	6.369	6.369
	C7	7.119	7.783	7.032
	C8	13.525	14.502	11.718
	C9	0.464	0.492	0.358
	C10	7.413	7.643	5.156
Mono-Aromatics	C11	0.171	0.173	0.108
	C6	0.473	0.404	0.600
	C7	4.163	3.601	4.471
	C8	4.851	4.178	4.522
	C9	20.543	17.606	16.916
	C10	2.946	2.516	2.189
	C11	2.451	2.086	1.636
Indenes	C12	0.981	0.746	0.599
	C10	0.149	0.116	0.114
	C11	0.676	0.526	0.457
Mono-Naphthenes	C12	0.307	0.239	0.190
	C5	7.524	7.570	10.618
	C6	1.081	1.072	1.272
	C7	1.576	1.560	1.588
n-Olefins	C8	0.598	0.494	0.528
	C5	1.325	1.532	1.870
Iso-Olefins	C6	0.968	1.064	1.138
	C5	1.684	1.921	2.376
	C6	1.035	1.132	1.217
	C7	0.320	0.342	0.376
Naphtheno-Olefins	C10	0.127	0.095	0.090
	C5	0.145	0.141	0.211

Recovery = 100.00

DETAILED HYDROCARBON ANALYSIS (DHA) REPORT OF FACE G GASOLINE

Hydrocarbon Expert V4.2	Thu Apr 02 11:21:35 2015	Page 2
File: C:\PIONA3\FT-0136A_FID2_B.CDF Sample: FT-00136A Parameter: C:\HPCHEM\HCE4\G95-OLEFIN_2015FID2_B LIMS Id:	2/22/2015 3:23:31 PM Operator: imran	

Composite by Carbon

<u>Group</u>	<u>C#</u>	<u>%Wgt</u>	<u>%Vol</u>	<u>%Mol</u>
Naphtheno-Olefins	C6	0.433	0.420	0.522
Oxygenates	C2	0.259	0.246	0.556

Recovery = 100.00

DETAILED HYDROCARBON ANALYSIS (DHA) REPORT OF FACE G GASOLINE

Hydrocarbon Expert V4.2	Thu Apr 02 11:21:35 2015	Page 1
File: C:\PIONA3\FT-0136A_FID2_B.CDF Sample: FT-00136A Parameter: C:\HPCHEM\HCE4\G95-OLEFIN_2015FID2_B LIMS Id:	2/22/2015 3:23:31 PM Operator: imran	

Calculated Boiling Point

<u>%Off</u>	<u>WBP(F)</u>
IBP	14.12
5%	73.63
10%	97.18
15%	115.32
20%	120.88
25%	144.26
30%	176.35
35%	193.99
40%	209.29
45%	210.17
50%	230.01
55%	233.90
60%	279.66
65%	307.19
70%	316.63
75%	324.43
80%	336.56
85%	336.74
90%	336.91
95%	369.50
FBP	405.15

Recovery = 100.00

DETAILED HYDROCARBON ANALYSIS (DHA) REPORT OF FACE G GASOLINE

Hydrocarbon Expert V4.2	Thu Apr 02 11:21:35 2015	Page 1
File: C:\PIONA3\FT-0136A_FID2_B.CDF Sample: FT-00136A Parameter: C:\HPCHEM\HCE4\G95-OLEFIN_2015FID2_B LIMS Id:	2/22/2015 3:23:31 PM Operator: imran	

Calculated Octane Numbers

<u>Group</u>	<u>RON</u>	<u>MON</u>
Paraffin	2.81	2.71
I-Paraffins	31.72	32.09
Aromatics	0.00	0.00
<i>Mono-Aromatics</i>	40.18	37.45
<i>Naphthalenes</i>	0.00	0.00
<i>Naphtheno/Olefino-Benz</i>	0.00	0.00
<i>Indenes</i>	1.43	1.29
Naphthenes	0.00	0.00
<i>Mono-Naphthenes</i>	10.31	8.86
<i>Di/Bicyclo-Naphthenes</i>	0.00	0.00
Olefins	0.00	0.00
<i>n-Olefins</i>	2.18	1.80
<i>Iso-Olefins</i>	3.12	2.63
<i>Naphtheno-Olefins</i>	0.54	0.42
<i>Di-Olefins</i>	0.00	0.00
Oxygenates	0.34	0.25
Unidentified	0.00	0.00
Plus	0.00	0.00

Total Linear RON = 92.64
Total Linear MON = 87.49

Total Calculated RON = 99.65
Total Calculated MON = 87.06

Recovery = 100.00

DETAILED HYDROCARBON ANALYSIS (DHA) REPORT OF FACE G GASOLINE

Hydrocarbon Expert V4.2	Thu Apr 02 11:21:35 2015	Page 1
File: C:\PIONA3\FT-0136A_FID2_B.CDF		2/22/2015 3:23:31 PM
Sample: FT-00136A		Operator: imran
Parameter: C:\HPCHEM\HCE4\G95-OLEFIN_2015FID2_B		
LIMS Id:		

Component List

Pk#	Time	Group	Component	%Wgt	%Vol	%Mol
1	7.747	I4	i-Butane	0.060	0.081	0.102
2	8.095	P4	n-Butane	2.793	3.618	4.756
3	8.703	X2	Ethanol	0.259	0.246	0.556
4	8.976	C5	3-Methylbutene-1	0.047	0.057	0.067
5	9.370	I5	i-Pentane	5.338	6.461	7.323
6	9.733	K5	Pentene-1	0.259	0.303	0.366
7	9.921	C5	2-Methylbutene-1	0.552	0.637	0.779
8	10.061	P5	n-Pentane	0.573	0.686	0.786
9	10.289	K5	t-Pentene-2	0.682	0.789	0.962
10	10.555	K5	c-Pentene-2	0.384	0.440	0.542
11	10.729	C5	2-Methylbutene-2	1.084	1.227	1.530
12	11.365	I6	2,2-Dimethylbutane	2.902	3.352	3.333
13	12.175	B5	Cyclopentene	0.145	0.141	0.211
14	12.749	M5	Cyclopentane	7.524	7.570	10.618
15	12.829	C6	2,3-Dimethylbutene-1	0.601	0.659	0.706
16	13.050	I6	2-Methylpentane	1.655	1.900	1.901
17	13.863	I6	3-Methylpentane	0.989	1.117	1.136
18	14.128	C6	2-Methylpentene-1	0.179	0.196	0.211
19	14.185	K6	Hexene-1	0.293	0.324	0.345
20	14.807	C6	2-Ethylbutene-1	0.062	0.067	0.073
21	14.871	P6	n-Hexane	0.398	0.453	0.457
22	14.991	K6	t-Hexene-3	0.126	0.138	0.148
23	15.171	K6	c-Hexene-3	0.258	0.282	0.303
24	15.325	K6	t-Hexene-2	0.291	0.319	0.342
25	15.555	C6	2-Methylpentene-2	0.193	0.209	0.227
26	15.813	B6	4-methylcyclopentene	0.144	0.141	0.173
27	16.255	C7	3-methyl-c-pentene-2	0.320	0.342	0.376
28	16.776	M6	Methylcyclopentane	0.801	0.803	0.942
29	17.052	I7	2,4-Dimethylpentane	1.393	1.553	1.376
30	18.667	B6	1-Methylcyclopentene	0.289	0.278	0.349
31	18.770	Q6	Benzene	0.473	0.404	0.600
32	19.648	M6	Cyclohexane	0.280	0.270	0.329
33	20.536	I7	2-Methylhexane	1.350	1.492	1.334
34	20.721	I7	2,3-Dimethylpentane	2.789	3.009	2.755
35	21.492	I7	3-Methylhexane	1.420	1.550	1.403
36	22.241	M7	1t,3-Dimethylcyclopentane	0.324	0.325	0.327
37	22.574	M7	1c,3-Dimethylcyclopentane	0.283	0.285	0.285
38	22.701	I7	3-Ethylpentane	0.166	0.178	0.164
39	22.905	M7	1t,2-Dimethylcyclopentane	0.240	0.239	0.242
40	23.075	I8	2,2,4-Trimethylpentane	8.164	8.848	7.074
41	24.543	P7	n-Heptane	1.100	1.207	1.087
42	27.444	M7	Methylcyclohexane	0.562	0.547	0.566
43	29.299	M7	Ethylcyclopentane	0.167	0.163	0.168

Recovery = 100.00

DETAILED HYDROCARBON ANALYSIS (DHA) REPORT OF FACE G GASOLINE

Hydrocarbon Expert V4.2	Thu Apr 02 11:21:35 2015	Page 2
File: C:\PIONA3\FT-0136A_FID2_B.CDF	2/22/2015 3:23:31 PM	
Sample: FT-00136A	Operator: imran	
Parameter: C:\HPCHEM\HCE4\G95-OLEFIN_2015FID2_B		
LIMS Id:		

Component List

Pk#	Time	Group	Component	%Wgt	%Vol	%Mol
44	29.519	I8	2,5-Dimethylhexane	0.504	0.545	0.437
45	29.674	I8	2,2,3-Trimethylpentane	0.222	0.232	0.192
46	29.829	I8	2,4-Dimethylhexane	0.717	0.767	0.621
47	32.416	I8	2,3,4-Trimethylpentane	2.740	2.857	2.374
48	33.074	Q7	Toluene	4.163	3.601	4.471
49	34.342	I8	2-Methyl-3-ethylpentane	0.600	0.631	0.519
50	35.434	I8	2-Methylheptane	0.431	0.464	0.374
51	35.696	I8	4-Methylheptane	0.147	0.156	0.127
52	36.756	M8	trans-1,3-dimethylcyclohexane	0.395	0.296	0.349
53	36.937	M8	1c,2t,3-Trimethylcyclopentane	0.203	0.198	0.179
54	38.707	I9	2,2,5-Trimethylhexane	0.464	0.492	0.358
55	41.593	P8	n-Octane	0.473	0.505	0.410
56	51.296	Q8	Ethylbenzene	0.640	0.554	0.597
57	53.439	Q8	m-Xylene	1.596	1.385	1.488
58	53.719	Q8	p-Xylene	0.615	0.536	0.574
59	59.266	Q8	o-Xylene	1.999	1.703	1.864
60	64.775	P9	n-Nonane	0.230	0.241	0.178
61	66.544	Q9	i-Propylbenzene	0.357	0.311	0.294
62	71.687	I10	C10 - IsoParaffin - 4	1.538	1.580	1.070
63	72.927	I10	3-Methyl-5-ethylheptane	5.534	5.713	3.849
64	73.221	Q9	1-Methyl-3-ethylbenzene	2.355	2.042	1.939
65	74.126	Q9	1,3,5-Trimethylbenzene	3.034	2.630	2.498
66	75.462	Q9	1-Methyl-2-ethylbenzene	2.388	2.033	1.966
67	75.782	I10	2-Methylnonane	0.171	0.176	0.119
68	76.677	I10	3-Methylnonane	0.171	0.175	0.119
69	77.585	Q9	1,2,4-Trimethylbenzene	10.409	8.912	8.571
70	80.013	C10	C10-iso-olefin-9	0.127	0.095	0.090
71	80.443	Q10	t-Butylbenzene	0.197	0.170	0.162
72	81.065	Q9	1,2,3-Trimethylbenzene	2.001	1.678	1.648
73	81.381	Q10	1-Methyl-3-i-propylbenzene	0.278	0.242	0.205
74	82.362	Q10	1,3-Dimethyl-5-ethylbenzene	0.623	0.531	0.460
75	84.553	Q10	1,4-Dimethyl-2-ethylbenzene	0.296	0.253	0.218
76	84.847	Q10	1,2-Dimethyl-4-ethylbenzene	0.722	0.620	0.533
77	85.261	Q10	1,3-Dimethyl-2-ethylbenzene	0.367	0.309	0.270
78	85.370	I11	C11 - IsoParaffin - 12	0.171	0.173	0.108
79	85.618	Q11	C11 - Aromatic - 1	0.645	0.544	0.431
80	86.501	Q11	1-Methyl-4-t-butylbenzene	0.221	0.195	0.147
81	87.614	Q11	1-Ethyl-4-i-propylbenzene	0.434	0.366	0.290
82	87.794	Q10	1,2,4,5-Tetramethylbenzene	0.463	0.391	0.341
83	88.420	J11	1H-Indene, 2,3-dihydro-1,2-dim	0.676	0.526	0.457
84	90.419	J10	3-methyl-Indene	0.149	0.116	0.114
85	91.630	Q11	1,3-diethyl-5-methyl benzene	0.304	0.268	0.203
86	91.952	Q11	1-Methyl-2-n-butylbenzene	0.428	0.360	0.286

Recovery = 100.00

DETAILED HYDROCARBON ANALYSIS (DHA) REPORT OF FACE G GASOLINE

Hydrocarbon Expert V4.2	Thu Apr 02 11:21:35 2015	Page 3
File: C:\PIONA3\FT-0136A_FID2_B.CDF Sample: FT-00136A Parameter: C:\HPCHEM\HCE4\G95-OLEFIN_2015FID2_B LIMS Id:		2/22/2015 3:23:31 PM Operator: imran

Component List

Pk#	Time	Group	Component	%Wgt	%Vol	%Mol
87	93.511	Q11	C11 - Aromatic - 11	0.293	0.259	0.196
88	94.429	Q12	C12-Aromatic-1	0.350	0.262	0.213
89	94.847	P12	n-Dodecane	0.182	0.181	0.106
90	96.997	Q12	Benzene, 3-ethyl-1,2,4,5-tetramethyl-	0.517	0.388	0.316
91	106.108	J12	Trimethyl Indene - 4	0.307	0.239	0.190
92	107.283	Q11	Pentamethylbenzene	0.126	0.094	0.084
93	114.574	Q12	1- Methyl-3-hexyl benzene	0.114	0.096	0.070

Recovery = 100.00

DETAILED HYDROCARBON ANALYSIS (DHA) REPORT OF FACE G GASOLINE

Hydrocarbon Expert V4.2	Thu Apr 02 11:21:35 2015	Page 1
File: C:\PIONA3\FT-0136A_FID2_B.CDF		2/22/2015 3:23:31 PM
Sample: FT-00136A		Operator: imran
Parameter: C:\HPCHEM\HCE4\G95-OLEFIN_2015FID2_B		
LIMS Id:		

Components by Group

Group	Time	Component	%Wgt	%Vol	%Mol
Paraffin	8.095	n-Butane	2.793	3.618	4.756
	10.061	n-Pentane	0.573	0.686	0.786
	14.871	n-Hexane	0.398	0.453	0.457
	24.543	n-Heptane	1.100	1.207	1.087
	41.593	n-Octane	0.473	0.505	0.410
	64.775	n-Nonane	0.230	0.241	0.178
	94.847	n-Dodecane	0.182	0.181	0.106
I-Paraffins	7.747	i-Butane	0.060	0.081	0.102
	9.370	i-Pentane	5.338	6.461	7.323
	11.365	2,2-Dimethylbutane	2.902	3.352	3.333
	13.050	2-Methylpentane	1.655	1.900	1.901
	13.863	3-Methylpentane	0.989	1.117	1.136
	17.052	2,4-Dimethylpentane	1.393	1.553	1.376
	20.536	2-Methylhexane	1.350	1.492	1.334
	20.721	2,3-Dimethylpentane	2.789	3.009	2.755
	21.492	3-Methylhexane	1.420	1.550	1.403
	22.701	3-Ethylpentane	0.166	0.178	0.164
	23.075	2,2,4-Trimethylpentane	8.164	8.848	7.074
	29.519	2,5-Dimethylhexane	0.504	0.545	0.437
	29.674	2,2,3-Trimethylpentane	0.222	0.232	0.192
	29.829	2,4-Dimethylhexane	0.717	0.767	0.621
	32.416	2,3,4-Trimethylpentane	2.740	2.857	2.374
	34.342	2-Methyl-3-ethylpentane	0.600	0.631	0.519
	35.434	2-Methylheptane	0.431	0.464	0.374
	35.696	4-Methylheptane	0.147	0.156	0.127
	38.707	2,2,5-Trimethylhexane	0.464	0.492	0.358
	71.687	C10 - IsoParaffin - 4	1.538	1.580	1.070
	72.927	3-Methyl-5-ethylheptane	5.534	5.713	3.849
	75.782	2-Methylnonane	0.171	0.176	0.119
	76.677	3-Methylnonane	0.171	0.175	0.119
	85.370	C11 - IsoParaffin - 12	0.171	0.173	0.108
Aromatics Mono-Aromatics	18.770	Benzene	0.473	0.404	0.600
	33.074	Toluene	4.163	3.601	4.471
	51.296	Ethylbenzene	0.640	0.554	0.597
	53.439	m-Xylene	1.596	1.385	1.488
	53.719	p-Xylene	0.615	0.536	0.574
	59.266	o-Xylene	1.999	1.703	1.864
	66.544	i-Propylbenzene	0.357	0.311	0.294
	73.221	1-Methyl-3-ethylbenzene	2.355	2.042	1.939
	74.126	1,3,5-Trimethylbenzene	3.034	2.630	2.498
	75.462	1-Methyl-2-ethylbenzene	2.388	2.033	1.966
	77.585	1,2,4-Trimethylbenzene	10.409	8.912	8.571
	80.443	t-Butylbenzene	0.197	0.170	0.162
	81.065	1,2,3-Trimethylbenzene	2.001	1.678	1.648

Recovery = 100.00

DETAILED HYDROCARBON ANALYSIS (DHA) REPORT OF FACE G GASOLINE

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Sample: FT-00136A		Operator: imran
Parameter: C:\HPCHEM\HCE4\G95-OLEFIN_2015FID2_B		
LIMS Id:		

Components by Group

Group	Time	Component	%Wgt	%Vol	%Mol
<i>Mono-Aromatics</i>					
	81.381	1-Methyl-3-i-propylbenzene	0.278	0.242	0.205
	82.362	1,3-Dimethyl-5-ethylbenzene	0.623	0.531	0.460
	84.553	1,4-Dimethyl-2-ethylbenzene	0.296	0.253	0.218
	84.847	1,2-Dimethyl-4-ethylbenzene	0.722	0.620	0.533
	85.261	1,3-Dimethyl-2-ethylbenzene	0.367	0.309	0.270
	85.618	C11 - Aromatic - 1	0.645	0.544	0.431
	86.501	1-Methyl-4-t-butylbenzene	0.221	0.195	0.147
	87.614	1-Ethyl-4-i-propylbenzene	0.434	0.366	0.290
	87.794	1,2,4,5-Tetramethylbenzene	0.463	0.391	0.341
	91.630	1,3-diethyl-5-methyl benzene	0.304	0.268	0.203
	91.952	1-Methyl-2-n-butylbenzene	0.428	0.360	0.286
	93.511	C11 - Aromatic - 11	0.293	0.259	0.196
	94.429	C12-Aromatic-1	0.350	0.262	0.213
	96.997	Benzene, 3-ethyl-1,2,4,5-tetramethyl-	0.517	0.388	0.316
	107.283	Pentamethylbenzene	0.126	0.094	0.084
	114.574	1- Methyl-3-hexyl benzene	0.114	0.096	0.070
<i>Naphthalenes</i>					
<i>Naphtheno/Olefins</i>					
<i>Indenes</i>					
	88.420	1H-Indene, 2,3-dihydro-1,2-dim	0.676	0.526	0.457
	90.419	3-methyl-Indene	0.149	0.116	0.114
	106.108	Trimethyl Indene - 4	0.307	0.239	0.190
<i>Naphthenes</i>					
<i>Mono-Naphthene</i>					
	12.749	Cyclopentane	7.524	7.570	10.618
	16.776	Methylcyclopentane	0.801	0.803	0.942
	19.648	Cyclohexane	0.280	0.270	0.329
	22.241	1t,3-Dimethylcyclopentane	0.324	0.325	0.327
	22.574	1c,3-Dimethylcyclopentane	0.283	0.285	0.285
	22.905	1t,2-Dimethylcyclopentane	0.240	0.239	0.242
	27.444	Methylcyclohexane	0.562	0.547	0.566
	29.299	Ethylcyclopentane	0.167	0.163	0.168
	36.756	trans-1,3-dimethylcyclohexane	0.395	0.296	0.349
	36.937	1c,2t,3-Trimethylcyclopentane	0.203	0.198	0.179
<i>Di/Bicyclo-Napht</i>					
<i>Olefins</i>					
<i>n-Olefins</i>					
	9.733	Pentene-1	0.259	0.303	0.366
	10.289	t-Pentene-2	0.682	0.789	0.962
	10.555	c-Pentene-2	0.384	0.440	0.542
	14.185	Hexene-1	0.293	0.324	0.345
	14.991	t-Hexene-3	0.126	0.138	0.148
	15.171	c-Hexene-3	0.258	0.282	0.303
	15.325	t-Hexene-2	0.291	0.319	0.342
<i>Iso-Olefins</i>					
	8.976	3-Methylbutene-1	0.047	0.057	0.067
	9.921	2-Methylbutene-1	0.552	0.637	0.779

Recovery = 100.00

DETAILED HYDROCARBON ANALYSIS (DHA) REPORT OF FACE G GASOLINE

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Sample: FT-00136A

Operator: imran

Parameter: C:\HPCHEM\HCE4\G95-OLEFIN_2015FID2_B

LIMS Id:

Components by Group

<u>Group</u>	<u>Time</u>	<u>Component</u>	<u>%Wgt</u>	<u>%Vol</u>	<u>%Mol</u>
<i>Iso-Olefins</i>	10.729	2-Methylbutene-2	1.084	1.227	1.530
	12.829	2,3-Dimethylbutene-1	0.601	0.659	0.706
	14.128	2-Methylpentene-1	0.179	0.196	0.211
	14.807	2-Ethylbutene-1	0.062	0.067	0.073
	15.555	2-Methylpentene-2	0.193	0.209	0.227
	16.255	3-methyl-c-pentene-2	0.320	0.342	0.376
	80.013	C10-iso-olefin-9	0.127	0.095	0.090
<i>Naphtheno-Olefins</i>	12.175	Cyclopentene	0.145	0.141	0.211
	15.813	4-methylcyclopentene	0.144	0.141	0.173
	18.667	1-Methylcyclopentene	0.289	0.278	0.349
<i>Di-Olefins</i>					
Oxygenates	8.703	Ethanol	0.259	0.246	0.556
Unidentified					
Plus					

Recovery = 100.00

DETAILED HYDROCARBON ANALYSIS (DHA) REPORT OF FACE G GASOLINE

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File: C:\PIONA3\FT-0136A_FID2_B.CDF

Sample: FT-00136A

Parameter: C:\HPCHEM\HCE4\G95-OLEFIN_2015FID2_B

LIMS Id:

2/22/2015 3:23:31 PM

Operator: imran

Calculated D86

<u>%Off</u>	<u>VBP(F)</u>
IBP	97.16
10.0%	123.93
20.0%	145.15
30.0%	165.96
50.0%	196.87
70.0%	287.84
80.0%	308.83
90.0%	323.49
FBP	365.86

Recovery = 100.00

DETAILED HYDROCARBON ANALYSIS (DHA) REPORT OF FACE G GASOLINE

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File: C:\PIONA3\FT-0136A_FID2_B.CDF Sample: FT-00136A Parameter: C:\HPCHEM\HCE4\G95-OLEFIN_2015FID2_B LIMS Id:	2/22/2015 3:23:31 PM Operator: imran	

Calculated Physical Properties

<u>Calculated</u>	<u>Total</u>
Avg MW	98.973
Avg SG	0.763
Avg API @ 60.0F	57.192
RVP (psi)	7.539
Tot H	13.495
C/H	6.409
Bromine Number	12.359
Aromatics with 6C (%weight)	0.000

Recovery = 100.00