Ignition delay times of Gasoline Distillation Cuts measured with Ignition Quality Tester

Nimal Naser[*], Eshan Singh, Ahfaz Ahmed, S. Mani Sarathy[*]
King Abdullah University of Science and Technology (KAUST),
Clean Combustion Research Center (CCRC), and,
Physical Science and Engineering Division (PSE). Thuwal, 23955-6900, Saudi Arabia

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 of various gasoline fuel distillation cuts are analyzed to better understand fuel properties of the full boiling range fuel. An advanced distillation column (ADC) provides a more realistic representation of volatility characteristics, which can be modeled using equilibrium thermodynamic methods. The temperature reported is that of the liquid, as opposed to the vapor temperature in conventional ASTM D86 distillation standard. Various FACE (fuels for advanced combustion engines) gasolines were distilled and various cuts were obtained. The separated fractions were then tested in an ignition quality tester (IQT) to see the effect of chemical composition of different fractions on their ignition delay time. Fuels with lower aromatic content showed decreasing ignition delay time with increasing boiling point (i.e., molecular weight). However, fuels with higher aromatic content showed an initial decrease in ignition delay time with increasing boiling point, followed by drastic increase in ignition delay time due to fractions containing aromatics. This study also provides an understanding on contribution of different fractions to the ignition delay time of the fuel, which provides insights into fuel stratification utilized in gasoline compression ignition (GCI) engines to tailor heat release rates.

Introduction

One novel approach to achieving global requirements for increased engine efficiency and lower overall greenhouse emissions is co-optimization of fuels and engines. In this regard, designing fuel to match engine requirements and operating conditions becomes imperative. One of the most informative and critical properties of commercial fuel is it's distillation curve. Standard distillation curve is measured by ASTM D86 [1] which is based on a gas burner heating the fuel and the evaporated compounds are cooled and collected. Commercial gasoline is a mix of several hundred compounds [2,3] and as such, there is no single boiling point. As different fractions of fuel are evaporated and subsequently cooled and collected, one gets a volume % versus temperature plot. The current standard method suffers from several drawbacks which have been dealt in detail by previous researchers [4]. For instance, there is lack of theoretical basis of the observed temperature values. The advanced distillation column (ADC) method, deviates from the standard and remedies some of the issues. The method provides lower uncertainty in temperature and volume measurements and a quantitative assessment of each distillate fraction and temperature values representative of true thermodynamic state. One of the highlights of the method used is the sampling of various distillation fractions. This enables an subsequent measurements

on the compositional effects of various fuel properties.

Burger et al. [5] studied the heat of combustion of various distillate fractions. Furthermore, it is one step towards better fuel design for achieving higher engine efficiencies. In this context, the current study aims to couple the advanced distillation column with an ignition quality tester (IQT) [6] to estimate the ignition delay times of separate volume fractions of various FACE (Fuels for Advanced Combustion Engines) gasoline [7]. The study aims to explicate the application of current distillation setup (physical property) in better understanding of its autoignition quality (physical-chemical kinetic property. The various boiling ranges can be correlated with the carbon chain length and the aromatic content of the compound, which in-turn dictates the autoignition tendency or ignition delay time of the fraction. This control the octane rating [8, 9] of the fuel, which is a bottleneck to current spark-ignition engine development.

Experiments

The section details the fuels and the experimental setups used in the present work. Four FACE (fuels for advanced combustion engines) [7] gasolines are used as given in Table 1. Due to potential candidacy of low octane (ON range of 70-85) fuels in the gasoline compression ignition engine concept [10], FACE I and J were used in the present work along with higher octane FACE fuels, FACE F and G that represent commercially available gasoline. Details on the composition of different FACE gasolines in volume percentage are also given in Table 1.

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[*]**Corresponding author: nimal.naser@kaust.edu.sa**
mani.sarathy@kaust.edu.sa

Table 1: Fuel properties

Fuel	FACE I	FACE J	FACE F	FACE G
RON	70.3	71.8	94.4	96.8
S	0.7	3	5.6	11
Density (kg/m3)	688	742	707	760
H/C	2.25	1.91	2.12	1.84
Stoichiometric AFR	15.03	14.56	14.85	14.46
Viscosity (cSt)	< 1.0			
n-paraffins (vol. %)	14.4	31.6	4.4	6.8
iso-Paraffins (vol. %)	74.5	33.6	67.5	38.5
Aromatics (vol. %)	1.2	31.7	7.7	33.7
Naphthenes (vol. %)	3.3	2.3	11	11.6
Olefins (vol. %)	6.4	0.6	9.4	8.2

The ADC measured distillations curve of the above fuels are shown in Fig. 1. From the figure it can be observed that how different compositions given in Table 1 influence the boiling points of different cuts of gasoline. The presence of aromatics causes the widest spread in boiling points due to their larger molecular weights.
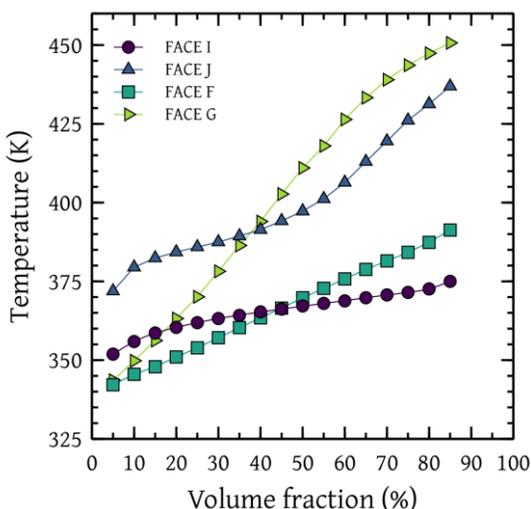

Figure 1: ADC measured distillation curve of FACE gasolines [5]

The distillation cuts of different gasolines were obtained with an advanced distillation column (ADC) that was commissioned with the help of Dr Bruno from National Institute of Standards and Technology (NIST) [4]. A schematic of the ADC equipment is given in Fig. 1 in [4]. The equipment consists of a round bottom flask [500 ml] that was heated with a aluminum heating jacket. To ensure temperature uniformity in the fluid a magnetic stirrer drive was placed beneath the aluminum jacket with a magnetic stir in the fluid. A distillation head with forced-air-cooled condensor placed above the round bottom flask to collect the distillate in a receiver. More details on the ADC method are provided in [4].

For the cuts used in the present work, 300 ml of FACE gasoline was placed in the round bottom flask and heated with the first 10 vol.% (i.e., 30 ml) of the distillate collected in the receiver transferred to a laboratory bottle. Standard ADC procedure [4] prescribes staring with 200 ml of fuel, but due to minimum requirements of 30 ml of fuel sample for the ignition quality tester (IQT), 300 ml was chosen. Similar procedures involved in obtaining the first cut was followed for the next 30 ml and so on to obtain 9 different cuts, the residue that remains (i.e. the last 10 vol. %) was not analyzed in the present work, so only cuts up to the T90 were studied. The cuts obtained were then measured in an IQT, details of which are presented below.

The KAUST research ignition quality tester (KR-IQT) is a constant volume combustion chamber that is filled with zero-air (20.9 $\pm$ 1.0 % O_2 and 79 % N_2 with trace quantities of hydrocarbons, < 1 ppm) pressurized to 2.137 $\pm$ 0.01 MPa and is heated to standard temperature prescribed by ASTM standard [11] into which liquid fuel is injected with a single-hole S-type inward opening pintle nozzle [12]. The standard temperature is obtained by a calibration procedure, that involves the adjustment of the chamber temperature such that average of 3 n-heptane runs provides an ignition delay of 3.78 $\pm$ 0.01 ms. The ignition delay is defined as the time difference between the start of injection (SoInj) and the start of ignition (SoIgn). The SoInj defined as the point where the needle lifts the maximum and the SoIgn is defined by the gradient method [13], the point of intersection of two line tangents. One line tangent being at the point where the chamber regains initial chamber pressure due to evaporative cooling of the liquid fuel spray and the other being at the maximum pressure rise due to ignition. More details on the gradient method and ignition delay definitions are available in [6,13]. The results presented below are the average ignition delay time of 32 injections and error bars indicate standard deviation of the readings

Results and discussion

The ignition quality of the various cuts obtained with the ADC method are analyzed in this section. Figure 2 shows the ignition delay times of various cuts of FACE I, with the first cut having the longest ignition delay time due to lighter alkanes having shorter chain lengths. Their largely iso-paraffinic nature leads to lower reactivity. For higher cuts the increasing chain length and n-paraffinic fraction leads

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to higher reactivity thereby shorter ignition delay times. This trend is observed until cut 7, for higher cuts the ignition delay times starts increasing due to heavier components in FACE I such as aromatics and naphthenes but their fraction is too low to cause any further increase in ignition delay time as observed in FACE J discussed later. The ignition delay time of full blend FACE I (6.91 ms) is also shown in Fig. 2.
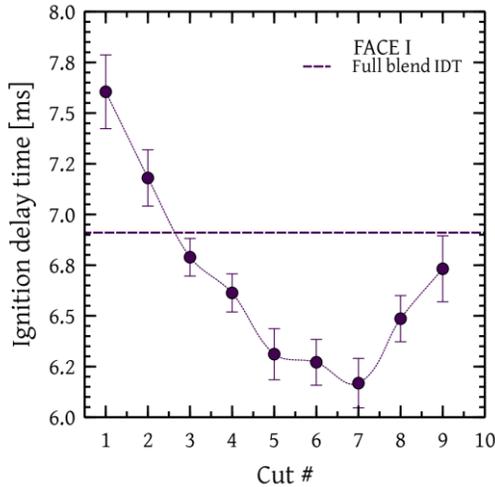

Figure 2: Ignition delay times of various cuts of FACE I gasoline

Ignition delay times of various cuts of FACE J gasoline are shown in Fig. 3, similar to FACE J, the ignition delay time of the first cut is longer than the middle cuts (2-7), however the last cuts have increasing ignition delay times due to increasing aromatic content (33.6 vol. %). The ignition delay time of the full blend FACE J (7.55 ms) is also shown. The average of the 9 cuts (12.19 ms) is also shown indicating that the linear by volume blending rules are not applicable in estimating ignition delay time. The inclusion of the last cut will only result in a higher average value of ignition delay time.
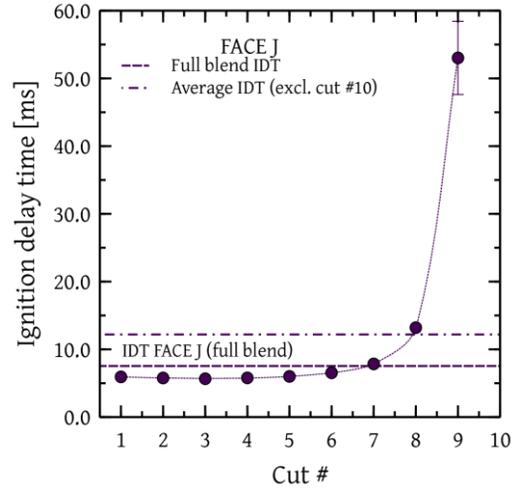

Figure 3: Ignition delay times of various cuts of FACE J gasoline

Next, high octane gasolines FACE F and G are analyzed. Figure 4 shows the ignition quality of FACE F cuts with moderate levels of aromatics indicating longer ignition delay time for the last cut. The first cut of FACE F gasoline has also relatively longer ignition delay times than the middle cuts (2-8) due to smaller chain alkanes known for their low reactivities. IDT of middle distillate cuts are shorter due to the presence of longer chain paraffins. The full blend ignition delay time of FACE F (14.74 ms) is also shown.
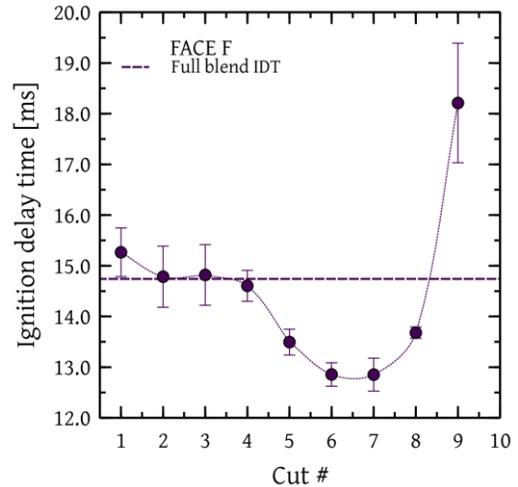

Figure 4: Ignition delay times of various cuts of FACE F gasoline

FACE G gasoline that has the widest spread in boiling points as observed in Fig. 5 and also has the widest spread in ignition delay times as can be seen in Fig. 5. Similar to all other gasolines the first cut has relatively longer ignition delay time than the full

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blend ignition delay time (15.99 ms). The middle cuts have lower ignition delay times due to increasing chain lengths, however the presence of one-third by volume of aromatics leads to increasing ignition delay times for the highest cuts. The average of the 9 cuts (25.5 ms) is also shown in Fig. 5, the inclusion of last cut would only shift the average to higher values. The deviation in the average and full blend ignition delay times indicate that the linear-by-volume is not the best approach in estimating the autoignition quality of fuels particularly involving aromatics due to the antagonistic nature of aromatics [14]. A more detailed study on the detailed composition of the different cuts using ^{1}H nuclear magnetic resonance (NMR) spectroscopy and how it influences the ignition quality using the methodology given in [15] is currently being pursued.
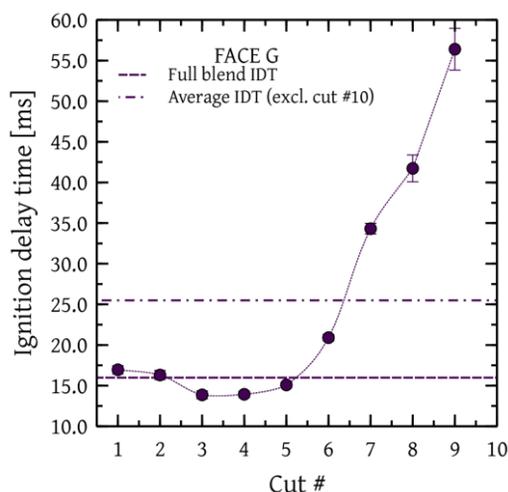

Figure 5: Ignition delay times of various cuts of FACE G gasoline

Concluding remarks

An advanced distillation column (ADC) was utilized in separating different fractions of carefully formulated gasoline test fuels known as FACE gasolines. The gasolines were separated on a volume basis by ADC method, with first cut being the first 10 vol. % obtained from the ADC, followed by the remaining cuts each being 10 vol. %. The last cut that contained the residue was excluded in the present study. The ignition quality of different cuts was then analyzed with an ignition quality tester to see the effect of chemical composition of different fractions on their ignition delay time. Fuels that had lower aromatic content showed decreasing ignition delay time with increasing boiling point with slight increase in ignition delay times in the last cuts due to lower

percentages of aromatics and naphthenes. However, fuels that had higher aromatic content showed an initial decrease in ignition delay time with increasing boiling point, followed by drastic increase in ignition delay time due to fractions containing aromatics. The linear-by-volume approach in measuring the ignition quality of full blend gasoline proved futile due to the antagonistic blending nature of aromatics. A careful examination of the detailed composition of the cuts using ^{1}H NMR spectroscopy is required to better understand the influence of various constituents of gasoline on its ignition quality.

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