

Derived Cetane Number, Distillation and Ignition Delay Properties of Diesel and Jet Fuels Containing Blended Synthetic Paraffinic Mixtures

Ulas Yildirim
RAAF, RMIT University

Renee Webster and David Evans
DST Group

Paul Rawson
DST Group, RMIT University

ABSTRACT

Aviation turbine fuel and diesel fuel were blended with synthetic paraffins produced via two pathways and the combustion properties measured. Both aviation and diesel fuel containing synthetics produced from the fermentation of sugars, had a linear response to blending with decreasing ignition delay times from 5.05 - 3.52 ms for F-34 and 3.84 - 3.52 ms for F-76. For the same fuels blended with synthetics produced from the fermentation of alcohols, ignition delay times were increased out to 18.66 ms. The derived cetane number of the blends followed an inversely similar trend. Additionally, simulated distillation using ASTM D2887 at high synthetic paraffinic kerosene blend ratios resulted in the recovery temperatures being incorrectly reported. In this case, higher recovery volumes were at lower temperatures than earlier recovery points i.e. $T_{90} < T_{50}$, for SIP-SPK.

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INTRODUCTION

Modern military vehicles utilise middle distillate fuels as a single fuel for compression ignition and gas turbine engines. There is a conflict between the volatility requirements and ignition delay requirements for jet fuels used for this purpose. Normally, cetane number does not constitute part of the jet fuel specifications but is measured for multifuel engine requirements. With the advent of synthetic fuels made from alternative feedstock there is increased control of fuel physicochemical requirements for the blend components.

It is impossible to define the exact composition of jet fuel. Hence, jet fuel specifications have evolved as performance specifications [1]. Moreover, in the past fuel specifications had materials and manufacture requirements limiting the feedstock to petroleum crude oil, natural gas condensates, heavy crude oil, shale oil, and oil sands [2]. The reason for the feedstock requirement is that not all properties of a fuel are listed in fuel specifications. Therefore, production of fuels from alternative feedstock may lead to changes in fuel performance due to a number of properties not being included in jet fuel specifications [2]. Original turbine aviation fuel specifications and properties were developed with the assumption that the fuel would be produced from crude oil [2]. Hence, the use of fuels from alternative sources cause a certain level of uncertainty requiring caution prior to their use. It is expected that new fuels will be drop-in

replacement to the currently approved fuels. As such, to prevent any issues during operation synthetic fuels are blended to approved percentages with conventional fuels depending on their feedstock.

Ignition delay (ID), along with other physical characteristics such as flame propagation, extinction and ignition, represent combustion properties dependent on fuel reactivity including volatility [3]. It has been reported that ignition delay is highly sensitive to fuel composition and structure, and can be deemed to be a good indicator of fuel reactivity variability and can be considered an appropriate target for the assessment of kinetic modeling schemes [3]. The physical characteristics of fuel including its ignition characteristics represent an important parameter in engine design [4]. The work of Dagaut and Cathonet provides a thorough review of the available data for the ignition, oxidation, and combustion of aviation fuels and surrogate mixtures [5]. Recent ignition delay time measurements incorporate heated shock tubes [6], rapid compression machines [7] and constant volume combustion chambers [8]. However, currently available kinetic models are incomplete and do not provide a correct description of the characteristics of ignition and combustion of surrogate modelling of real aviation fuels in wide ranges of temperatures, pressures, and mixture compositions [9]. Therefore, understanding kinetic chemical behaviour of alternative fuels through ignition delay and other parameters is needed to more accurately kinetic modelling.

Cataluna and da Silva reported that ‘ignition delay times are influenced by several phenomena associated with the nature of the fuel such as molecular structure, volatility, viscosity etc. with the fuels’ volatility having a significant influence on the ignition delay time’ [10]. Moreover, Ghosh and Jaffe note that fuels with high concentrations of *n*-paraffins generally have low ignition delay times [11]. Conversely, *iso*-paraffins and aromatics have been reported to have longer ignition delay times attributed to their more stable molecular structures requiring higher activation energies to start the combustion process [10].

It has been reported that fuels with low volatility and high cetane numbers generate larger fuel droplets due to their higher viscosities. This leads to fuel entering further into the flame zone, causing incomplete combustion, and increasing emissions of unburned hydrocarbons and particulate matter [10]. Distillation profiles provide further evidence on the fuel’s performance. The temperature of 10% of the volatilized gas fractions recovered reflects the ease of vaporization, while the temperature of 90% of these fractions indicates the presence of high molecular weight compounds that will be difficult to vaporize completely [10, 12].

A fuel’s volatility is an important parameter highlighting its tendency to form a fuel-air mixture prior to combustion. Vapor pressure and distillation profile are the two physical properties used to estimate its volatility. A more volatile fuel has a higher vapor pressure and lower initial distillation temperatures [13]. It has been reported that vapor pressure limits were developed in conjunction with front-end distillation limits. Although, the two properties have been shown to be interrelated, ‘compositional effects and measurement scatter mitigate against an accurate estimation of vapor pressure based on distillation data’ [14]. A direct relationship exists between molecular size and volatility of hydrocarbons affecting their boiling points [15]. Fuel volatility is controlled by specification limits derived from distillation data based on the ASTM D86 test for distillation of petroleum products [16].

There is little data in the literature pertaining to the impact of blended synthetic fuels on combustion properties. Zheng *et al.* demonstrated the response of Sasol iso-paraffinic kerosene (IPK) versus conventional ultra-low sulfur diesel (ULSD) to cetane improver addition using an Ignition Quality Tester (IQT) [17]. Cetane number (CN) is a measure of the ignition quality of the diesel fuel and can be determined by standard engine test methods as specified by ASTM D613 and ASTM D6890 [18, 19]. The ignition quality is quantified by measuring the ignition delay time, which commences with the injection of the fuel and the start of combustion of the fuel. An inverse relationship between CN and ignition delay time exists meaning short ignition delay periods are assigned to fuels with high CN [11].

Ghosh and Jaffe have reported trends of cetane variation across each hydrocarbon class as a function of the number of carbon atoms in the molecule, as well as structural differences [11]. Cetane number was greatest for *n*-alkanes and increased with carbon number whilst the

presence of aromatics reduced the cetane number. Some of the simpler molecular components such as the *n*-paraffins can ignite in an internal combustion engine easier due to their simple molecular bonds, but others such as aromatics require higher temperatures and pressures for ignition which then directly affects the cetane number of the fuel [11]. Allen *et al.* reported that synthetic paraffinic kerosene (SPK) is known to have higher cetane numbers due to the lack of aromatics in the fuel [20]. Conventionally manufactured aviation and diesel fuels contain aromatics, which provide benefits in preventing seal swell and shrinkage of fuel-wetted parts.

Derived cetane number (DCN) provides a global indication on the chemical reactivity of a fluid [21]. As such, any undocumented variations in ignition delay times are expected to cause problems possibly leading to damage to internal engine components [22]. Similarly, aircraft gas turbines have requirements regarding ignition such as a gas turbine’s ability to reignite during possible wind milling conditions [23]. In the same vein as internal combustion engines, increased ID times can be problematic for gas turbines during re-light if not well established and documented.

As the test fuels are relatively new, reliable information concerning the applicability and behavior of these fuels is required such that engine designers and manufacturers are given the opportunity to tailor the operating parameters of their equipment. Hence, it is important that the test fuels’ thermo-physical properties are well observed and documented. To enable this, various methods and equipment are available in determining ignition delay of liquid hydrocarbons including constant volume bombs, reciprocating engines and steady flow test apparatus.

Zheng *et al.* highlighted that the autoignition process includes overlapping physical and chemical processes that have been known to be difficult to ascertain in diesel engines due to the complexity of the combustion chamber geometry. Moreover, determining the exact effect of charge temperature and pressure within an engine is difficult to ascertain due to the fact that compressed air properties vary during combustion. These are no longer a concern with constant volume vessels such as the IQT within which the changes in the charge temperature and pressure during the ID period are much smaller than in real engines. Finally, the IQT brings advantages in running these autoignition tests by the fact that very little fuel is required for the tests and the whole setup is automated removing operator error [8].

This paper investigates DCN and ID in a constant volume chamber as well as simulated distillation profile to observe fuel combustion properties using minimal volumes of research fuels that are not widely available for testing [24].

EXPERIMENTAL

Fuels

The aviation fuels used met the requirements for Jet A-1 containing a military additive package (NATO Code F-34 or US JP-8) [25]. The diesel fuel used was naval grade (NATO Code F-76) with improved

water shedding capability as well as enhanced storage stability [26]. These were sourced from various Defence bases in Australia. Synthetic paraffinic kerosenes (SPK) were produced by the Alcohol To Jet (ATJ) and the synthesised *iso*-paraffins from hydroprocessed fermentable sugars (SIP) pathways. These were both supplied by the Fuels Division at US NAVAIR (Maryland, USA). Blends of conventional fuels with the synthetic components were carried out using standard laboratory glassware in increasing 10 % v/v aliquots.

Derived Cetane Number and Ignition Delay Testing

The ignition delay time and DCN measurements were carried out using a bench scale IQT (Advanced Engine Technology Ltd., Ottawa, Canada) for both fuel blends. The tests were carried out in accordance with ASTM D6890 by Intertek Australia [19]. The IQT is a bench-scale device. A detailed description is provided by Zheng et al [8]. In simple terms the IQT has a constant volume combustion chamber with external electrical heating elements, a fuel injection system, an intake system, an exhaust system, a data acquisition system, and a cooling system [8]. The combustion chamber is preheated to the standard test temperature by nine cartridge-type resistance heaters. The fuel is then compressed and delivered by a pneumatically driven mechanical fuel pump into the combustion chamber [8].

Aviation fuel and diesel (referred to as F-34 and F-76 respectively) were blended with ATJ-SPK and SIP-SPK. These fuels were tested for derived cetane number, distillation profile and ignition delay response to increasing SPK content. The derived cetane number is calculated by the relationship with ignition delay in a constant volume vessel (equation 1).

$$\text{DCN} = 4.46 + (186.6/\text{ID}) \quad (1)$$

For fuels that have ID shorter than 3.1 ms or longer than 6.5 ms, the DCN can be calculated with less precision from equation 2 below.

$$\text{DCN} = 83.99 \times (\text{ID} - 1.512) - 0.658 + 3.547 \quad (2)$$

Due to the limited sample size atmospheric distillation profiles using classic techniques (ASTM D86) was not possible. In order to determine the distillation profile, a simulated method using as gas chromatography (GC) method (ASTM D2887) was used.

Simulated Distillation

The instrumentation used for GC simulated distillation analyses was an Agilent 7890A-5975C GCMS (Agilent Technologies, Santa Clara, USA) using parameters defined in ASTM D2887. The dataset was solved using SimDist Application as part of the DVLS PetroReporter software (Da Vinci Laboratory Solutions, Rotterdam, The Netherlands) which uses the coefficients in ASTM D2887 [27] to provide a distillation profile correlating to ASTM D86 [28]. Recovery points not calculated in the software were calculated using the coefficients in ASTM D2887 (Table X5.1). The method assigns

boiling points from a calibration curve obtained under the same chromatographic conditions by analyzing a known mixture of hydrocarbons covering the boiling range expected in the sample.

RESULTS

IQT Results

The base aviation fuel was blended with ATJ-SPK and SIP-SPK in 10 % v/v increments to neat SPK (Figures 1 and 2). For ATJ-SPK, the blend volume being suggested in the aviation sector is up to 50 % v/v. For SIP-SPK the approved blend volume no greater than 10 % v/v [29]. ATJ-SPK is limited by aromatic content of the finished fuel, whilst SIP-SPK concentration is limited due to the low temperature viscosity requirement of the finished fuel. In this instance it is noted that the two alternative fuels behave differently as the volume of the alternative fuel increases. For SIP-SPK, the ID times decrease from 5.05 ms for F-34 and 3.84 ms for F-76. For ATJ-SPK, the ID times increase affecting the DCN for each fuel due to the relationship shown in equation 1. The neat SPKs have ID times of 3.52 ms (SIP-SPK) and 18.66 ms (ATJ-SPK).

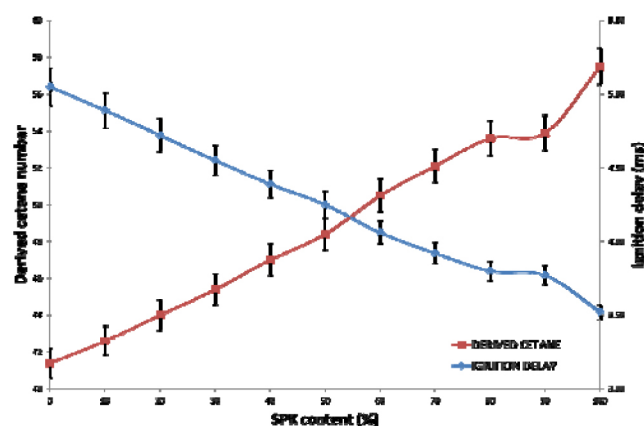


Figure 1. Derived cetane number and ignition delay for F-34 blends of SIP-SPK

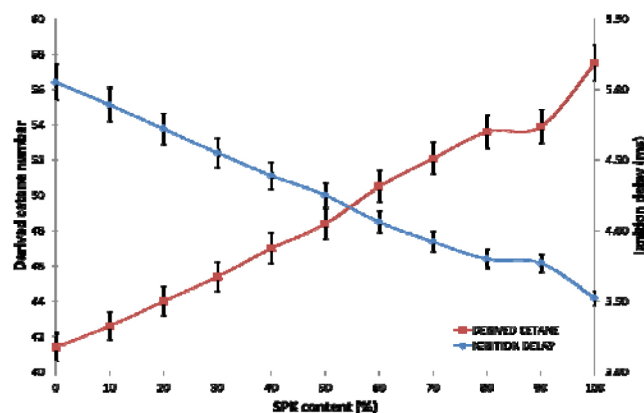


Figure 2. Derived cetane number and ignition delay for F-34 blends of ATJ-SPK

Unlike the aviation sector, there is little to no guidance on the amount of synthetic component allowed in diesel fuels. Due to the operational requirements by most navies, a certification process similar to the aviation sector is utilized to ensure the fuel is truly a 'drop-in'.

replacement. Currently, ATJ-SPK and SIP-SPK pathways are being investigated with a blend percentage of 50 % and 20 % v/v respectively. Testing of the synthetic blends with F-76 showed comparable trends for both SIP-SPK and ATJ-SPK as to those observed in F-34 albeit with higher starting DCN and shorter ID values (Figures 3 and 4).

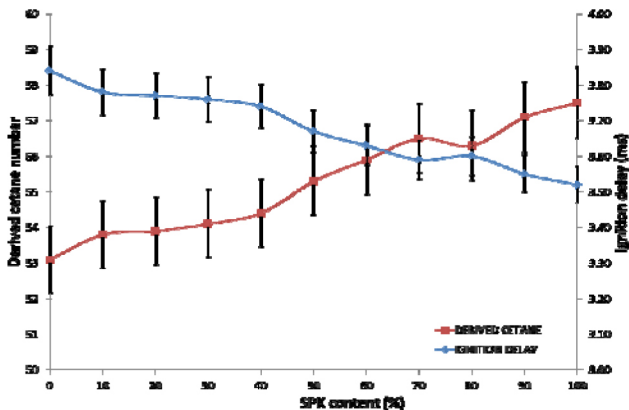


Figure 3. Derived cetane number and ignition delay for F-76 blends of SIP-SPK.

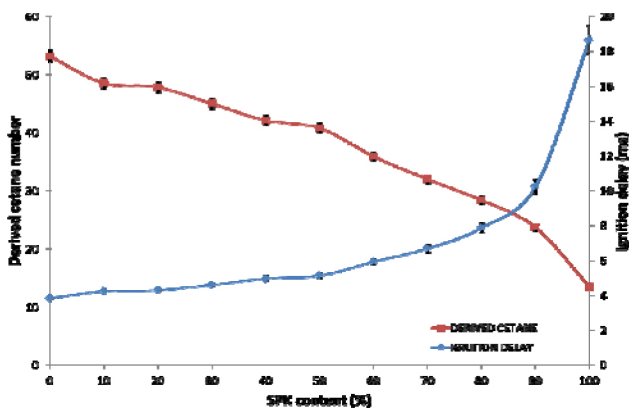


Figure 4. Derived cetane number and ignition delay for F-76 blends of ATJ-SPK.

Simulated Distillation

Distillation profiles for both the jet and diesel blends were performed using the GC method and subsequent correlation to D86 [28]. For conventional jet fuels, the volume recovered defined by T_{10} , T_{50} and T_{90} as well as the final boiling point (FBP) are reported with limits for T_{10} and FBP (205 °C and 300 °C respectively) [25]. Fuels containing synthetic components such as FT-SPK or HEFA-SPK are required to meet these limits after blending [29].

The distillation profile for diesel fuels varies between specifications with reporting levels and limits focused around the heavier end of the distillation profile [26]. The jet fuel distillation profile limits are aimed at ensuring relight during any flight profile whereas the limits in diesel are to reduce emissions and particulate matter. Whilst volume recovered temperatures are reported only the T_{10} , T_{50} and T_{90} are shown in the tables.

Chromatograms shown in Figure 5 highlight the differences between the conventional fuels and SPKs. Whilst the conventional fuels exhibit a bell curve-like distribution, the SPKs demonstrate a reduced distribution and in the case of SIP-SPK the dominance of a single component. Tables 1, 2, 3, 4 highlight the impact of distribution and hence volatility upon blending of conventional fuels and SPKs.

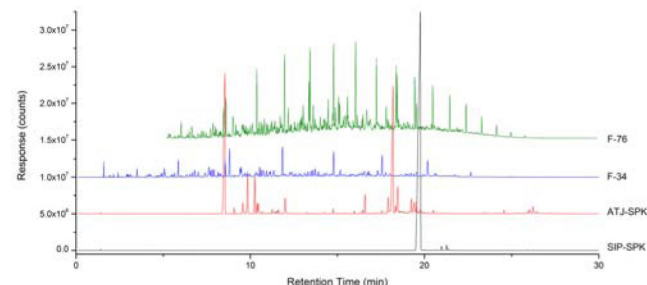


Figure 5. GC/MS chromatograms for F-34, F-76, ATJ-SPK and SIP-SPK. Y axis has been offset.

Simulated Distillation Profile of Aviation Blends

The SIP-SPK blends met the distillation requirements of aviation fuel specifications up to a 70 % v/v concentration with the 80 % v/v T_{10} temperature exceeding 205 °C (Tables 1 and 2). The results indicate an issue with the D2887 method and synthetic fuel with narrow distillation profiles. At 50 % v/v there is an inversion of the data with T_{90} being less than T_{50} . This remains an issue for all subsequent blends up to neat SIP-SPK. For recovery temperatures above T_{50} , the D86 values were used with the D2887 data reported in bracket of table 1.

Table 1. Simulated distillation values correlated to ASTM D86 for SIP blends with F-34. Values in brackets are D2887 derived where correlation errors occurred.

% SPK	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)	$T_{90}-T_{10}$ (°C)	$T_{50}-T_{10}$ (°C)
0	160	177	205	46	17
10	164	184	228	64	20
20	165	189	235	71	25
30	167	201	236	69	34
40	170	214	237	66	44
50	174	239	247 (237)	73 (62)	65
60	181	242	247 (237)	66 (56)	60
70	192	245 (246)	247 (237)	55 (45)	53 (53)
80	224	245 (246)	247 (238)	23 (14)	21 (22)
90	242 (247)	245 (246)	247 (239)	5 (-10)	3 (-1)
100	242 (264)	245 (247)	247 (239)	5 (-25)	3 (-17)