

Binary Mixtures of Branched and Aromatic Pure Component Fuels as Surrogates for Future Diesel Fuels

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ABSTRACT

Future synthetic diesel fuels will likely involve mixtures of straight and branched alkanes, possibly with aromatic additives to improve lubricity and durability. To simulate these future fuels, this study examined the combustion characteristics of binary mixtures of 50%, 70%, and 90% isododecane in hexadecane, and of 50%, 70%, and 80% toluene in hexadecane using a single-cylinder research diesel engine with variable injection timing. These binary blends were also compared to operation with commercial petroleum diesel fuel, military petroleum jet fuel, and five current synthetic Fischer-Tropsch diesel and jet fuels. The synthetic diesel and jet fuels showed reasonable similarity with many of the combustion metrics to mid-range blends of isododecane in hexadecane. Stable diesel combustion was possible even with the 80% toluene and 90% isododecane blends; in fact, operation with 100% isododecane was achieved, although with significantly advanced injection timing. As the concentration of toluene in hexadecane increased, combustion was either stable or progressed quickly to misfire; 80% toluene in hexadecane resulted in stable combustion but 85% toluene blends did not combust at all. With either blend, there was not a progressive change in peak pressure, maximum rate of pressure rise, or combustion phasing leading to extreme values. Instead, only modest changes in these metrics occur as blend fraction changes across a wide range. Increasing blend fraction of either component does steadily increase ignition delay, although 50% mixtures of either component cause only a modest change in ignition delay. Increasing blend fraction also increases the amount of fuel consumed in the rapid premixed combustion phase, although estimation of this fraction showed that it increases even more slowly than ignition delay

with increasing concentration. Only when ignition delay is longer than approximately 1.8 ms does the amount of energy released from the premixed-phase burn show significant increase. The increasing fraction of the branched or aromatic component causes changes to the mixture properties that can reduce the rate of entrainment and mixing in the diesel jet, partially compensating for small increases in ignition delay. Mixture properties for each blend were measured using standardized testing procedures, including tests for density, viscosity, surface tension, and cetane number. The results suggest that blends of up to 50% of branched or aromatic components could be utilized in a diesel engine with only modest impact to combustion characteristics or performance metrics; higher concentrations may be utilized with increasing effects.

INTRODUCTION

The Fischer-Tropsch (FT) fuel conversion process offers the opportunity to produce alternative sources of liquid hydrocarbon (HC) fuels for transportation. However, all FT synthetic fuels are not created equal. Variations in fuel feedstock, process conditions, and catalyst materials can lead to different fuel character, notably in the fraction of different hydrocarbon structures that exist in the fuel. FT fuels are comprised of principally two hydrocarbon structures, “normal” or “straight-chain” alkanes and “iso-” or “branched” alkanes. One common characteristic of FT synthetic fuels, however, is their lack of sulphur and aromatic content, and thus FT fuel is often characterized as “cleaner” due to the absence of these two important soot precursors.

Conventional HC based fuels for diesel and jet engines can be characterized as mixtures of five different hydrocarbon classes: straight-chain alkanes, branched alkanes, cyclic

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alkanes, aromatic, and alkene hydrocarbons. Diesel fuel has been shown to have approximately equal amounts of straight-chain alkanes, aromatics, and cyclic alkanes with a minority fraction of branched alkane species [1]. Jet fuel (Jet A) has been shown to contain over 50% straight and branched alkanes, with another 25% of the fuel coming from cyclic alkanes (mono-, di- and tri-). The final minority fraction (up to 25%) was shown to be aromatic species [2].

FT based fuels, on the other hand, are principally comprised of straight-chain and branched alkanes. Both of these HC fuel structures have lower density than aromatic compounds, and thus FT fuels have lower densities overall when compared with conventional petroleum jet and diesel fuels. Of the currently available commercial FT based fuels, there exists considerable variability in composition. One study compared five different FT (jet) fuels from three different manufacturers [3]. The branched alkane content varied from twenty-five to nearly ninety percent. The distribution of the branched alkanes from C8 to C18 also varied significantly with C10 to C14 being the approximate mean of the different fuels.

Diesel engines are unique in that they are able to burn both jet and diesel fuels. The military often uses jet fuel in diesel engines due to the logistical simplicity of having only one tactical fuel. Jet fuel is the choice for both diesel and jet engines, since the high boiling range of diesel fuel is not compatible with the typically cold operating environment of aircraft.

With such a wide range of FT fuel compositions that are being considered for use in diesel engines, there is an important need to understand the relative importance of straight-chain and branched alkane structures in diesel combustion. How do pure components with these structures, as well as mixtures of these two structures, behave in a diesel engine? Does combustion become too delayed with significant branched alkane (low cetane) composition?

Additionally, an improved understanding of the relative importance of aromatics in diesel fuel is also essential, but not well understood. Addition of aromatic fuel species to FT fuels is likely to be required for fuel system component (notably fuel pump) durability [4]. Due to the low cetane nature of aromatic fuel species, it is critical to understand the limits of aromatic content in diesel fuel and to determine to what extent aromatic content addition affects the combustion characteristics of a diesel engine.

The objective of this study is to address these basic questions for branched and aromatic content in diesel fuels by testing two different binary mixtures: The first binary mixture is hexadecane (C₁₆H₃₄, straight-chain alkane) with isododecane (2,2,4,6,6-pentamethylheptane, C₁₂H₂₆, a highly branched

alkane). This binary mixture could be a reasonable surrogate for future synthetic jet and diesel fuels given that many FT synthetic blends are largely composed of normal and branched saturated alkanes. The second binary mixture is hexadecane with toluene (C₇H₈, an aromatic species). This mixture serves to simulate the addition of aromatics to future synthetic fuels. Hexadecane, isododecane, and toluene were chosen both due to their ease of availability and also that there exist chemical reaction mechanisms for these species that are either well-established or under development. Other studies of simplified fuel surrogates have suggested the use of similar species. For example, Farrell et al. recently proposed a detailed plan to build surrogate mixtures to approximate the behavior of diesel fuel to aid in detailed modeling of advanced diesel engines. They proposed using simple mixtures of straight chain, branched, cyclic, and aromatic components including hexadecane and toluene [5].

Pure components or simple mixtures are not only used to approximate the behavior of complex mixtures, but the simplified fuels themselves can often be used to elucidate the behavior of the more complex mixtures. Stanglmaier et al. used single pure components, binary mixtures, and more complex mixtures to study the effects of wall-wetting in DI gasoline engines [6]. In the mid 1980s, Glavinčevski tested hundreds of pure component fuels using ¹H NMR spectroscopy to better understand the connection between molecular structure and cetane number [7]. Caton et al. (including several of the authors of this work) recently studied twenty-one pure component fuels, including straight chain alkanes and alkenes, branched alkanes, cyclic alkanes and alkenes, and aromatic species, focusing on the effects of fuel property variation on ignition delay [8]. In contrast to using simplified fuels to represent more complex ones, Janssen et al. recently published their efforts to design an optimum fuel for a diesel engine by optimizing the cetane number, boiling point, and molecular structure of the mixture using blends of iso-octane and heptane, decalin, heptane, and dodecane [9].

EXPERIMENT

ENGINE AND DATA ACQUISITION

The engine used in this study is a standard single-cylinder Cooperative Fuels Research (CFR) diesel test engine. The speed is fixed with a motoring/absorbing dynamometer at 900 RPM. The engine allows variable compression ratio, injection timing, and injection amount. Table 1 lists the basic specifications of this engine and the operating conditions used in this study. A Kistler™ 6125B pressure transducer was mounted in the engine head. Airflow was measured with a laminar flow element. A line diagram of the engine configuration is shown in Figure 1. Data were collected with a National Instruments™ LabView data acquisition system sampling at a rate of 50 kHz.

Table 1. Experimental engine parameters.

Type	Indirect-injection diesel, pancake-style chamber, in-line cam-driven pump
Bore	82.6 mm
Stroke	114 mm
Speed	900 RPM fixed
Compression Ratio	18
Coolant	water reflux, 100°C
Intake Air	Lab ambient, 20°C
Fuels	hexadecane ($C_{16}H_{34}$) – baseline isododecane ($C_{12}H_{26}$)-hexadecane (50%, 70%, 90% by vol.) toluene (C_7H_8)-hexadecane (50%, 70%, 80% by vol.) commercial diesel U.S. Navy JP-5 synthetic diesel and jet fuel (5 blends)

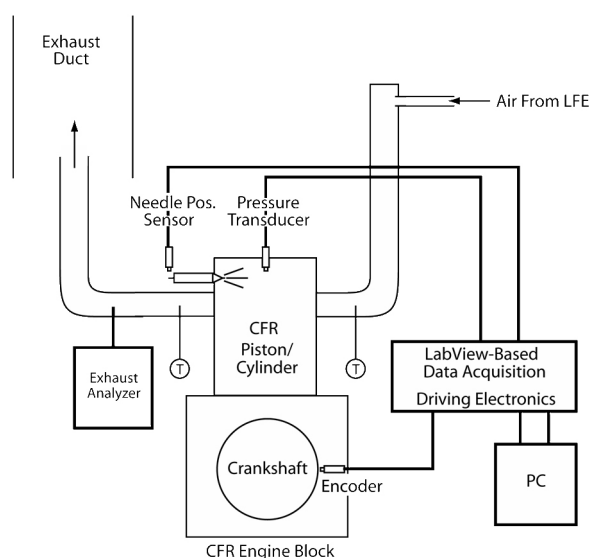


Figure 1. Schematic of experimental diesel CFR engine

ENGINE TESTING

The diesel CFR engine is designed for fuels testing. In its stock configuration, it utilizes a rotary valve to switch between a system of three small fuel tanks. In this study, the binary mixture of either isododecane-hexadecane or toluene-hexadecane was added to the first fuel tank. Testing a particular mixture began with a flushing procedure as follows: First, a small amount of the fuel blend of interest was added to the first fuel tank and combustion was stabilized with this fuel blend. Then, the tank, injection pump, fuel metering buret, and associated lines were drained. Once the engine stopped firing, all of the fuel lines had been emptied of the fuel blend. This procedure was repeated a second time, with a second drainage step. Finally, approximately 0.5 - 0.75 L of the fuel blend of interest was added to the first tank and to the fuel buret. The fuel was metered by direct volume measurement over approximately 60 seconds of engine operation using the fuel buret. Prior to data collection, the engine was operated with the fuel blend until steady operation was achieved.

Testing began by adjusting fuel delivery to achieve 3.5 ± 0.05 bar gross indicated mean effective pressure (GMEP) at the lowest (most retarded) possible injection timing setting for the engine. Typically, this resulted in start of injection (SOI) timing around 13° before top-center (BTC). The GMEP and SOI were determined by averaging 40 engine cycles using the data acquisition system described above. Five different injection advance settings were tested, typically achieving SOI between 13° and 23° BTC. As injection timing was adjusted, the fuel delivery was adjusted simultaneously to

Exhaust gas was analyzed using a steady-state analyzer system and sampled from the exhaust flow using a heated filter approximately 10 cm downstream of the combustion chamber using a five-gas Infrared Industries™ FGA4000XD exhaust gas analyzer. Hydrocarbons (HC), carbon dioxide (CO_2), carbon monoxide (CO) were measured using a non-dispersive infrared process while oxygen (O_2) and nitric oxide (NO) were measured using an electrochemical cell method. Exhaust gas was sampled on a dry basis through a non-heated line; only NO emissions data are reported in this study.

maintain 3.5 ± 0.1 bar GMEP. In this study, operating points were grouped together as “retarded” with injection timing $13^\circ \pm 0.5^\circ$ BTC, “nominal” with injection timing $15^\circ \pm 0.5^\circ$ BTC, and “advanced” with injection timing $20^\circ \pm 0.5^\circ$ BTC. In most cases, the “retarded” timing condition actually produced the lowest fuel consumption; the labels are only meant as descriptors relative to the adjustment range of the engine, and are not meant to suggest reference to best-torque timing. Due to limitations on the extent of fuel injection timing adjustment, optimized best-torque timing was not always possible to achieve with the various tested fuel blends. However, the injection timings shown in this study are representative of typical diesel injection timings. Once the desired load and injection timing were achieved, each operating point was maintained for several minutes to ensure stable combustion and emissions measurements.

FUELS AND BINARY MIXTURE PREPARATION

Binary mixtures of isododecane-hexadecane and toluene-hexadecane were prepared using a 1 L volumetric flask (± 0.3 mL accuracy) and a 1 L graduated cylinder (± 3.0 mL accuracy). All blends were prepared on a volumetric basis. Combining the accuracy of all volume measurements, the largest expected error is $\pm 0.2\%$ on the cited concentration (e.g. $70\% \pm 0.2\%$).

Hexadecane was acquired from Sigma-Aldrich with specified purity $> 99\%$. The isododecane used in this study was acquired from KIC Chemicals and is a mixture of $C_{12}H_{26}$ isomers with specified purity of 98% minimum. The toluene was acquired from Chevron Phillips with a specified purity of 99.5% minimum. A comprehensive listing of the pure component fuels and fuel blends tested is shown in [Table 2](#). Two conventional fuels (commercial diesel and U.S. Navy JP-5, neat) and five synthetic fuels (neat) were included for comparison with the simple binary mixtures.

Cetane number was determined for all tested fuels using a variety of methods. By definition, pure hexadecane has a cetane number of 100. For 50% and 80% blends of toluene with hexadecane, cetane number was measured in-house using the diesel CFR test engine and the ASTM D613 test specification with hexadecane and heptamethylnonane as primary reference fuels [10]. The cetane number for isododecane and toluene were used as cited in [Ref. \[11\]](#). This NREL report cites the cetane number of isododecane as 9 as supported by two independent studies [12,13]. There is disagreement over the cetane number of toluene, with cited values ranging from -5 to 18.3 . In this study, the literature value of -5 (from [Ref. \[13\]](#)) is adopted as it agrees very well with the measured cetane number of the toluene blends. Finally, measurements of the cetane number and lower heating value of the commercial diesel, JP-5, and the five synthetic blends were provided by the Fuels Division of the

Naval Air Systems Command using the ASTM D976 and ASTM D4809 testing specification [14, 15]. The lower heating value for pure components and binary mixtures was calculated based on published enthalpy of formation data [16].

The liquid fuel density and kinematic viscosity of all fuels in this study were measured in-house using a SVM 3000 Stabinger Viscometer (Anton Paar) at 20.00°C . For each fuel, at least two samples were analyzed. The accuracy of the measurement system was tested with a certified viscosity reference standard (Standard 83, Cannon Instrument Company). The percent difference between the measured and actual values at 20.00°C was less than 1.4% for viscosity and less than 1% for density. The precision of the instrument was determined from duplicate samples, and the percent deviation from the mean was found to be less than 1%.

A Kruss DS100 drop shape analyzer was used to measure the liquid-air surface tension of the fuels. In this analyzer, a droplet of the fuel is formed in the air with a microsyringe. The system then takes an image of the droplet, enlarges it, and analyzes the droplet shape by fitting it with the Young-LaPlace equation. The measured value for toluene, 27.9 mN/m at 22°C , is similar to the reported value of 27.93 mN/m at 25°C [17].

[Table 2](#) gives the liquid-air surface tension, liquid kinematic viscosity, liquid density, and cetane number data of the fuels used in this study along with associated accuracy specifications. Distillation profiles were not measured in this study, but are also of interest for assessing the effect of fuel property changes on combustion characteristics. Atmospheric boiling point temperatures for hexadecane, isododecane, and toluene are 281°C , 178°C , and 111°C (data from [Ref. \[16\]](#)).

ENERGY RELEASE ANALYSIS

A single zone heat release analysis was used in this study [18,19,20]. This analysis is useful to characterize start of combustion and burn durations. Start of injection (SOI) was determined from an injector position sensor. Start of combustion (SOC) was determined analytically as the 10% fuel burned state. Ignition delay was then determined analytically as the difference between SOI and SOC. The 50% mass fraction burned location (CAD50) is used as an indicator of combustion phasing.

The premixed fraction was defined as the ratio of extent of premixed combustion phase to the total combustion duration. Premixed fraction was calculated using two different bases: First, using a time basis, premixed fraction was the ratio of the premixed combustion phase duration to the total combustion duration, using time or crank-angle degrees (CAD). Second, on an energy basis, premixed fraction was calculated as the mass fraction burned at the end of the

Table 2. Selected properties of tested fuels and fuel blends at 20°C

Class and Formula		σ^1 (mN/m)	ν (mm ² /s)	ρ^2 (kg/m ³)	cetane	LHV (MJ/kg)	Notes
Baseline Fuel							
n-hexadecane	(C ₁₆ H ₃₄)	26.3	4.47 ± 0.003	774	100	43.9	
Branched Alkane Reference							
isododecane	(C ₁₂ H ₂₆)	21.4	1.75 ± 0.0007	749	9	46.1	4
Aromatic Reference							
toluene	(C ₇ H ₈)	27.9	0.656 ± 0.0002	867	-5	40.5	5
Binary Mixtures (by volume)							
50% isododecane in hexadecane		23.3	2.77 ± 0.002	761	-	45.0	
70% isododecane in hexadecane		22.5	2.32 ± 0.003	756	-	45.5	
90% isododecane in hexadecane		21.7	1.93 ± 0.004	751	-	45.9	
50% toluene in hexadecane		26.6	1.31 ± 0.0009	817	62.3	42.3	6
70% toluene in hexadecane		27.1	0.953 ± 0.0005	836	-	41.6	
80% toluene in hexadecane		27.4	0.831 ± 0.0003	846	19.7	41.3	3, 6
Conventional Fuels							
Diesel	C _{13.5} "D"	26.9	3.94 ± 0.005	856	44	42.6	7
JP-5	C _{12.2} "J"	24.9	1.85 ± 0.001	800	46.2	43.2	7
Synthetic Fuels							
"STF" (FT)	C _{11.0} "1"	28.3	2.75 ± 0.018	865	21.3	42.6	7
"Lansol 50" (FT)	C _{13.4} "2"	25.8	3.79 ± 0.002	778	72.8	N/A	7
"Sasol" (FT)	C _{14.2} "3"	25.3	3.98 ± 0.010	772	76.1	N/A	7
"Shell GTL" (FT)	C _{9.4} "4"	22.6	1.18 ± 0.013	733	57.9	42.5	7
"S5" (FT)	C _{11.6} "5"	23.5	2.14 ± 0.001	760	67.1	44.5	7

1Accuracy specifications for surface tension are ± 0.1 mN/m for all measurements.

2Accuracy specifications for density are ± 0.1 kg/m³ for all measurements.

3Surface tension value for 80% toluene blend interpolated from 70% toluene blend and measured value for 85% toluene blend (27.6 mN/m).

4Cetane number of isododecane from Refs. [12, 13] as cited in Ref. [11].

5Cetane number of toluene from Ref. [13] as cited in Ref. [11]; note that Ref. [11] cites disagreement in the literature as to the actual cetane number of toluene. Cited values range from -5 to 18.3.

6Cetane numbers of 50% and 80% toluene-hexadecane blends measured in-house using the ASTM D613 specification [10].

7Estimation of carbon number based on measured hydrogen content and estimation of molecular weight based on interpolation between similar, known blends or from correlations of boiling point data. Procedure described in Ref. [8]. Cetane number measurements using ASTM D976 specification [14] from Fuels Division of Naval Air Systems Command, Patuxent River, MD.

premixed combustion phase. Both metrics require the estimation of the premixed combustion phase. A typical energy release profile is shown in Figure 2 which illustrates the premixed combustion phase and the two calculation methods. Mathematically, the end of the premixed combustion phase was set at the first local minimum in energy release after the peak energy release such that

successive local minima demonstrated a decrease in energy release of less than a certain threshold. This threshold was approximately 10% and was tuned by inspection of many energy release profiles so that the algorithm worked well to capture the initial energy release peak usually attributed to the premixed phase [18].