The combustion properties of 2,6,10-trimethyl dodecane and a chemical functional group analysis

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ABSTRACT

The global combustion characteristics of 2,6,10-trimethyl dodecane (trimethyl dodecane), a synthetic fuel candidate species, have been experimentally investigated by measuring extinction limits for strained laminar diffusion flames at 1 atm and reflected shock ignition delays at 20 atm. The Derived Cetane Number (DCN) of trimethyl dodecane, (59.1) and Hydrogen/Carbon (H/C) ratio (2.133) are very close to the DCN and H/C ratio of a previously studied synthetic aviation fuel, S-8 POSF 4734 (S-8) and its surrogate mixture composed of n-dodecane/iso-octane (58.9 and 2.19, respectively). Identical high temperature global kinetic reactivities are observed in all experiments involving the aforementioned compounds. However, at temperatures below ∼870 K, the S-8 surrogate mixture has ignition delay times approximately a factor of two faster. A chemical functional group analysis identifies that the methylene (CH_2) to methyl (CH_3) ratio globally correlates the low temperature alkylperoxy radical reactivity for these large paraffinic fuels. This result is further supported experimentally, by comparing observations using a surrogate fuel mixture of n-hexadecane (n-cetane) and 2,2,4,4,6,8,8-heptamethyl nonane (iso-cetane) that shares the same methylene-to-methyl ratio as trimethyl dodecane, in addition to the same DCN and H/C ratio. Measurements of both diffusion flame extinction and reflected shock ignition delays show that the n-cetane/iso-cetane model fuel has very similar combustion behavior to trimethyl dodecane at all conditions studied. A kinetic modeling analysis on the model fuel suggests the formation of alkylhydroperoxy radicals (QOOH) to be strongly influenced by the absence or presence of the methyl and methylene functional groups in the fuel chemical structure. The experimental observations and analyses suggest that paraffinic based fuels having high DCN values may be more appropriately emulated by further including the CH_2 to CH_3 ratio as an additional combustion property target, as DCN alone fails to fully distinguish the relative reaction characteristics of low temperature kinetic phenomena.

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1. Introduction

Concerns regarding the finite and potentially insecure nature of crude oil supplies, allied with global warming caused by carbon dioxide emissions, have led to growing interest in renewable liquid transportation fuels. Alternative liquid fuel production methodologies using a range of fossil energy sources, such as coal and natural gas, are gaining popularity. Nevertheless, approaches using renewable resources, such as animal fats, plant oils, or ligno-cellulosic biomass materials [1,2], can further augment and/or replace fossil energy sources while reducing net carbon emissions.

Whilst the molecular composition of alternative synthetic fuels are notionally similar to some components of the complex mixtures that constitute petroleum derived aviation and diesel fuels, the absence from alternative synthetic fuels of the large variety of molecular structural classes and molecule sizes, marks them as a fuel class different to traditional liquid fuels. An example of particular significance is that synthetic fuels do not generally contain aromatic components as a significant fraction [3–5]. Such peculiarities are pertinent to fuel certification standards, as these requirements and test procedures have evolved within the historical experience of traditional crude oil derived fuels and engine propulsion technologies rather than from a fundamental scientific understanding of the combustion process [3–5]. Thus, a more scientific characterization of synthetic fuel properties and their combustion performance in comparison to those of the historical

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fuels they may augment or replace is necessary. Such knowledge can aid in the development of efficient and effective methodologies for the certificate of alternative fuels.

Recently, gas turbine fuel certification standards [6] have been modified to encompass blending of up to fifty percent bio-derived synthetic fuel components from hydroprocessed esters and fatty acids (HEFA, from vegetable oil-containing feedstocks such as algae, Camelina or Jatropha, or from animal fats, i.e. Tallow) or Fischer Tropsch hydroprocessed synthetic paraffinic kerosine (F-T-SPK, from coal, natural gas or biomass) [3–5,7]. Among other emerging process options that yield renewable fuel candidates, Amyris Corporation has developed a fermentation procedure to convert biomass materials through the isoprenoid metabolic pathway into farnesene isomers. Subsequent hydrogenation produces an entirely pure enantiomeric mixture of farnesane (2,6,10-trimethyl dodecane) which is under consideration as both an alternative diesel or aviation fuel [8]. The molecular structure of 2,6,10-trimethyl dodecane is depicted in Fig. 1.

Further knowledge of how new alternative fuel candidates can be at least initially screened for gas turbine fuel applications, without large quantities of materials or expensive, large scale, prototype testing typical of the certification process for FT-SPK and HEFA fuels would be very beneficial. In this regard, significant insights have been made through researching concepts for formulating surrogate component mixtures to emulate real fuel combustion properties [9–11]. Our recent studies [9–11] have shown that the fully pre-vaporized global combustion characteristics of a targeted multi-component jet fuels can be well characterized by emulating four "combustion property targets" of the fuel of interest: (1) Hydrogen to Carbon molar ratio (H/C ratio), (2) Derived Cetane Number (DCN) from the Ignition Quality Tester (IQT), (3) average molecular weight (MW), and (4) Threshold Sooting Index (TSI). In a wide range of fundamental combustion experiments, the fully pre-vaporized combustion properties of surrogate mixtures, formulated using the aforementioned combustion property targets, were experimentally compared against specific real fuels. These experiments included ignition delay times from a reflected shock tube and a rapid compression machine, laminar flame speeds, strained extinction of premixed and diffusion flames in the counterflow configurations, and speciation profiles from a flow reactor and shock tube. The results demonstrated excellent fidelity for the performance of the formulated surrogate mixtures against the targeted fuels [9–11].

In addition to demonstrating the above approach for emulating petroleum derived jet fuels, we also investigated the sufficiency of these criteria for determining surrogate mixtures for a real F–T synthetic jet fuel, derived from natural gas by Syntroleum Inc. [11]. This fuel, designated more generally in the literature as "S-8" (The particular sample that we analyzed was POSF 4734), contains no aromatic fraction and large percentages of mono and di-methylated, weakly branched alkanes. A simple surrogate fuel composed of only n-dodecane and iso-octane was formulated and experimentally shown to closely emulate the vapor phase combustion kinetic behavior of the target S-8 fuel. In the same study, combustion property targets were shown to be effective in emulating a single component mono-methylated alkane, 2-methyl heptane, though it is noted that comprehensive testing was not performed [11]. The proposition of 2,6,10-trimethyl dodecane as a pure, chemically definite fuel or fuel component presents an additional opportunity to investigate the effectiveness of the combustion property target approach as a surrogate formulation strategy. The results of the experimental characterizations presented here are discussed in this context.

2,6,10-Trimethyl dodecane (hereafter referred to as "trimethyl dodecane"), with its uniquely branched character, can potentially influence global combustion behavior differently than the more weakly branched mono and dimethylated alkanes found in S-8 or iso-octane used in earlier surrogate formulations. The hydrogen/carbon ratio and molecular weight are explicitly defined by the molecular formula, leaving only the Derived Cetane Number (DCN) and the Threshold Sooting Index (TSI) as property targets to be experimentally determined. As most alkane flames have very high smoke points [12,13] beyond the detection limit of the smoke point test, ASTM D 1322 [14], the TSI is neglected in the subsequent analysis as a weakly sensitive parameter. From the procedures described below, the DCN of trimethyl dodecane is determined in this work as 59.1 ± 0.6. As shown in Table 1, trimethyl dodecane shares the same DCN (within the experimental precision of ±0.6) as determined previously for the gas-to-liquid synthetic aviation fuel, S-8 (POSF 4734, DCN = 58.9) [11]. Additionally, as for all large paraffinic fuels, the H/C values are also very similar, leaving only the (average) molecular weight as a parameter significantly different between the two fuels.

Previous studies [9–11] concluded that the influence of molecular weight metric is mostly upon diffusion limited combustion [15–17]. As a result, the gas phase combustion characteristics of trimethyl dodecane are expected to be similar to those of S-8 (and an n-dodecane/iso-octane surrogate mixture) under premixed conditions, but may differ somewhat under diffusion-limited circumstances. Analysis of the combustion properties of trimethyl dodecane relative to those of S-8, thus presents a serendipitous opportunity to further the scientific understanding of fuel properties and test the combustion property targets determined thus far for defining the combustion reactivity of complex hydrocarbon mixtures against the more constrained situation presented by a chemically pure fuel. The potential of 2,6,10-trimethyl dodecane as a chemically-definitive species, rather than the very complex and variable mixtures of fuel components (as synthetic and historical liquid fuels are), presents a further challenge to the effectiveness of the combustion property targets as a surrogate formulation strategy or as an initial characterization tool for the combustion behaviors of proposed alternative fuels.

Here, we present an experimental characterization of trimethyl dodecane in terms of its strained diffusive extinction and autoignition properties. These properties are experimentally compared against those of S-8 (POSF 4734) and with a surrogate fuel mixture of n-hexadecane (n-cetane) and 2,2,4,4,6,8,8-heptamethyl nonane (iso-cetane) that shares the same methyl-to-methylene ratio as trimethyl dodecane (in addition to the same DCN and H/C ratio). The results of the experimental characterization of trimethyl dodecane are discussed in the context of behaviors relative to S-8 POSF 4734 surrogate and the n-cetane/iso-cetane model fuel. A kinetic modeling analysis for the n-cetane/iso-cetane model fuel is also pursued to elucidate the relationship of methylene/methyl functional group ratio to the formation of alkylhydroperoxy radical (QOOH) at low temperatures. The experimental observations and analyses suggest that paraffinic based fuels having high DCN values may be more appropriately emulated by incorporating the methylene/methyl functional group ratio as an additional combustion property target, as DCN alone fails to fully distinguish the characteristics of low temperature kinetic phenomena.

2. Experiments

The design and operational methodologies of the counter flow diffusion flame burner at *Princeton University* and the high pressure shock tube at *Rensselaer Polytechnic Institute* have been thoroughly
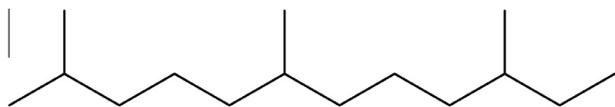

Fig. 1. Molecular structure of Farensane or 2,6,10-trimethyl dodecane.