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Chemical ignition delay of candidate drop-in replacement jet fuels under fuel-lean conditions: A shock tube study

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ABSTRACT

Ignition delay times were measured behind reflected shock waves under fuel lean, high pressures conditions for conventional (JP-8) and alternative jet fuels --- Fischer-Tropsch (F-T), alcohol to jet (ATJ), direct sugar to hydrocarbon (DSHC), and four bio-jet — and a biodiesel-like fuel. The primary goal of this study was to investigate the effect of fuel structure on ignition delay in order to assess differences in fuel ignition delay relative to JP-8. To support this effort, the ignition characteristics of a few hydrocarbons that are proposed as jet fuel surrogate components were also investigated: n-heptane, n-dodecane, m-xylene, n-dodecane/m-xylene blend (77%/23% by volume) and 2,2,4,6,6-pentamethylheptane (iso-dodecane). Two single-pulse shock tubes (heated and non-heated) were used to obtain the current data set. Using argon as the diluent (93% by volume), the experimental conditions covered a pre-ignition temperature range of approximately 980–1800 K at a pressure of 16 \pm 0.8 atm and an equivalence ratio of 0.5. Experimental results show negligible differences between the ignition delay times of JP-8, F-T, DSHC, biodiesel, and the four bio-jet fuels. They are very similar to those of n-heptane, ndodecane, n-dodecane/m-xylene blend and iso-dodecane under similar conditions. However, the ignition delay times of the ATJ were slightly longer at higher temperatures, and similar to iso-dodecane. m-Xylene reported significantly longer ignition delay times than the other fuels tested under identical conditions. Kinetic modeling results show that light branching and carbon chain length of large *n*-paraffins do not alter ignition delay because the predominant reactions are oxidation of C_1 - C_4 fuel fragments. They also show for the *n*-dodecane/*m*-xylene blend that a discernable slowing of ignition delay by fuel decomposition and oxidation of m-xylene occurs at mxylene concentrations greater than 50% (by mol.). Further testing is required to understand this behavior at stoichiometric and fuel rich conditions. In addition, an empirical correlation was obtained between the global activation energy of the measured ignition delay times for the single paraffinic species and their derived cetane numbers. This contributes to recent efforts aimed to provide relationships between pre-vaporized, homogeneous combustion properties with existing combustion indicators.

1. Introduction

The aviation industry has seen an increased interest within the recent past for developing and certifying alternative, nonpetroleum-derived jet fuels. The main reasons are the price uncertainty and dwindling availability of petroleum-based fuels, dependencies on foreign oil sources and pollutant emissions [1,2]. Several approaches are being investigated to determine the feasibility of using alternative jet fuels in near-, mid- and long-term scenarios. In the near-term, only blends of alternative and conventional petroleum-based fuels (*e.g.*, Jet-A and JP-8) have been approved as "drop-in" fuels (*i.e.*, fully interchangeable with conventional jet fuels without requiring any substantial modifications to the engine or aircraft) after significant evaluations of the alternate jet fuel [2,3].

Approved alternative fuels for blending in conventional fuel at different concentrations include Fischer-Tropsch (F-T) processed fuels, hydroprocessed esters and fatty acids (HEFA) (formerly called hydrotreated renewable jet fuels (HRJ)), [4–6] alcohol-to-jet (ATJ) fuels [7],

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and direct sugar to hydrocarbon (DSHC) fuels [8]. Biodiesel [5] is an alternative fuel for diesel fueled engines, but considered a contaminant in aviation fuel (50 ppm by vol max). F-T fuels are typically produced using coal, natural gas or biomass, whereas HEFA fuels are produced via thermochemical treatments such as hydrodeoxygenation or hydrogenation of animal fats, vegetable oil or bio-crude (typically extracted from renewable feedstocks such as lignocellulosic feedstock, swine manure or microalgae [9]). The direct sugar to hydrocarbon process, recently developed by Amyris Biotechnologies Inc., employs fermentation of bio-sugars (i.e. sugar cane) into hydrocarbons by genetically modified micro-organisms [10]. The resultant hydrocarbons undergo further hydrotreatment processes resulting in 2,6,10-trimenthyldodecane, also known as farnesane [10]. The term biodiesel refers to a blend of alkyl esters of long chain fatty acids produced by transesterification of vegetable or animal fats [5]. With the exception of biodiesel, all the above-mentioned alternative fuels are highly paraffinic. Dagget et al.² used the term "bio-jet" to indicate biomass-derived jet fuel that is particularly adapted for aviation standards.

For all drop-in fuels, a careful examination of ignition and relight characteristics is critical to flight safety; high altitude operation and lean blowout limit are among the major technological challenges associated with the use of alternative fuels [11]. Relighting the engine at high altitudes is more difficult than at low altitude conditions because the lower air supply and lower temperatures prevent effective fuel atomization and vaporization. Thus, the ignition characteristics become extremely important at high altitude relight conditions [12]. Blowout occurs when the residence time within the combustor is too short to guarantee the normal evolution of chemical reactions [13]. Blowout correlations relate blowout limits to the ratio of characteristic chemical time and residence time. While the latter is merely dependent on the combustor design, the chemical time is intrinsically related to the fuel composition. Consequently, investigation of ignition delay time provides valuable information for blowout and relights [13,14].

Limited experimental data are available for ignition delay measurements of alternative jet fuels. The most investigated synthetic isoparaffinic jet fuel (referred to as S-8) was produced by Syntroleum via the F-T process. In previous work of our group, ignition delay times of S-8 and JP-8 were measured behind reflected shock waves under fuel lean conditions ($\Phi = 0.5$) [14]. The experiments covered a pre-ignition temperature range of 1000-1600 K at a pressure of 20 atm. Gokulakrishnan et al. [15] used an atmospheric pressure flow reactor to investigate ignition delay times of S-8 and JP-8 between 900 and 1200 K at lean (Φ = 0.5) and rich (Φ = 1.5) conditions. While these studies report similar ignition delay times for JP-8 and S-8, a recent investigation by Kumar and Sung [16] shows that S-8 ignites faster than JP-8 under similar conditions of pressure, temperature and air-to-fuel mass ratio. In the Kumar and Sung work, experiments were carried out using a rapid compression machine covering a pre-ignition temperature range of 650-933 K, a compressed charged pressure of 7, 15 and 30 bars and an air-to-fuel mass ratio of 13 and 19. Zhu et al. [17] measured ignition delay times of fifteen alternative fuels and two distillate jet fuels behind reflected shock waves. Experimental conditions covered a pre-ignition temperature range of 1047-1520 K, two pressure ranges of 2.07-8.27 atm and 15.9-44.0 atm, equivalence ratios in the range of 0.25-2.2 and two mixture regimes including fuel/air and fuel/4% oxygen/argon. In their study, under all conditions, iso-paraffinic fuels and conventional fuels reported similar ignition delay times. However, the ATJ showed a lower reactivity compared to HEFA and F-T fuels. Won et al. [18] investigated global combustion characteristics of 2,6,10-trimethyldodecane (farnesane) in terms of ignition delay times behind reflected shock waves (pre-ignition temperatures in the range of 690-1250 K, pre-ignition pressure of 20 atm and stoichiometric fuel/air mixture), extinction limits of laminar diffusion flames and derived cetane numbers (DCN). Results collected for farnesane were compared with surrogate mixtures including an S-8 surrogate (n-dodecane/isooctane, 51.9/48.1 mol%) and n-cetane/iso-cetane (45.9/54.1 mol%).

Similar ignition delay times and derived cetane numbers (59.1) were observed between farnesane and the *n*-cetane/*iso*-cetane mixture. Min et al. [19] measured ignition delay times for Jet-A, farnesane and ATJ in a rapid compression machine over a pre-ignition temperature range of 600–700 K, pressure of 20 bar and equivalence ratios of 1.0, 0.5 and 0.25. ATJ, whose DCN is 15, reported the longest ignition delay times. Farnesane appeared to be the more reactive among the fuels with the shortest ignition delay times. To the authors' knowledge, no gas-phase ignition delay measurements have been reported for a practical biodiesel jet fuel; however, efforts have been made to find viable surrogates that are able to reproduce similar combustion behavior of oxygenated fuels [20–24].

Shock tubes are an established experimental tool used to measure ignition delay under operating conditions relevant to modern gas turbines [25]. They offer a unique advantage with effectively no complications originating from physical (e.g., mixing, atomization and vaporization) and fluid dynamical effects involved in an actual combustion process. They also provide insight into the effects of pressure and temperature on chemical kinetics [26]. The current study used single-pulse reflected shock tubes to investigate the chemical ignition delay of homogeneous gas-phase mixtures (pre-vaporized and premixed prior to ignition). The primary goal of this investigation was to understand the effects of fuel composition on ignition delay for several alternative jet fuels. The composition of the fuels tested is provided in Table 1 and Figs. 1 and 2. Nine formulated fuels were studied: a conventional jet fuel (JP-8), a coal-derived F-T from Sasol, a DSHC from Amyris Biotechnologies Inc., an ATJ from GEVO, a biodiesel fuel, and bio-jet fuels derived from corn grain (bio-jet 1), canola (bio-jet 2) and soy (bio-jets 3 and 4).

As is evident from Table 1 and Fig. 1, paraffinic hydrocarbons (normal and branched) are major constituents of all the fuels tested. Aromatics are also present in significant quantities for JP-8. The F-T fuel consists of *iso*-paraffins and a small amount of cycloparaffins. Similarly, the ATJ fuel from GEVO (produced via oligomerization of *iso*-butanol) is mainly comprised of 2,2,4,6,6-pentamethylheptane (*iso*-dodecane) and 2,2,4,4,6,8,8-heptamethylnonane (*iso*-cetane) with negligible amount of cycloparaffins and aromatics. The DSHC is a single component fuel solely consisting of farnesane. The biodiesel is a mixture of various alkyl esters (Table 1), with butyl esters being the most abundant. The carbon distributions in Fig. 2 show that the major constituents of these fuels are in the range of C₁₀-C₁₂. All the fuels, excluding bio-jet 1 (corn grain), bio-jet 3 (soy), the biodiesel and the ATJ, have a normal carbon distribution.

To further investigate the nature of fuel composition effects on ignition delay, additional experiments of *n*-heptane, *n*-dodecane, *iso*-dodecane, *m*-xylene and an *n*-dodecane/*m*-xylene blend (77/23:% liquid volume) were carried out. Molecular structures of the selected single component surrogates are showed in Table 2. *n*-Dodecane and *m*-xylene were chosen since they have previously been proposed in jet fuel surrogates to represent the paraffinic and aromatic components, respectively; the blend composition was chosen based on the recommendation of previous work [27]. *n*-Heptane was chosen to observe the effect of *n*paraffin chain length on ignition delay (*i.e.*, comparison with *n*-dodecane), in addition to the compound being studied elsewhere as a potential gasoline surrogate [28]. *iso*-Dodecane was selected as it is the major constituent of the ATJ fuel.

Kinetic modeling was performed to further understand the experimental results. A kinetic model based on USC Mech II [29], JetSurf v. 1.0 [30] and UIC *m*-xylene oxidation model 2 [31] was used to simulate the ignition delay times for the pure hydrocarbons and the 2-component blend. This model is a combination of efforts performed under the Strategic Environmental Research and Development Program (SERDP) projects for modeling of potential JP-8 surrogate blend. A recent study [32] on ethylene combustion showed that a small deviation from experimental measurements is observed at higher pressures. *n*-Heptane and *n*-dodecane ignition delays were also modeled using the Download English Version:

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