Ignition Delay Study of Low Reactivity Fuel Blends

Kyungwook Min

Department of Zero-carbon Fuel & Power Generation, Korea Institute of Machinery & Materials
Daejeon, Korea
&
Keunsoo Kim, Tonghun Lee
Department of Mechanical Science and Engineering, University of Illinois
Urbana, Illinois, US

1   Introduction

Fuel reactivity is one of the key characteristic parameters of fuel combustion. A mixture of fuel and oxidizer under autoignition condition ignites after certain amount of time – ignition delay time (IDT). The length of IDT is a function of various parameters; temperature, pressure, equivalence ratio, and chemical composition of the fuel. By examining fuel sensitivity to IDT under various conditions, the autoignition behavior under varying fuel supply scenarios can be better understood. Unwanted sudden autoignition in an intermittent combustion engine could result in engine knock, leading to critical failure of the engine and vehicle. Small scale unmanned aerial vehicles (UAVs) equipped with compression ignition (CI) engines suffer from engine knock due to the combination of extreme ambient operating environments and the fluctuating properties of supplied fuels. Unlike CI engine equipped ground vehicles, which primarily run on diesel fuels, kerosene aviation fuels are the major type of fuels consumed in UAVs. Since jet fuels are mostly utilized in continuous combustion engines, studies on autoignition reactivity of jet fuels are relatively scarce. So far, cetane number (CN) rating is widely used to characterize the autoignition reactivity of diesel fuels. CN rating can be also used for jet fuels as an indicator of autoignition reactivity. A detailed understanding of jet fuel autoignition propensities is needed to improve aviation compression ignition engine reliability and performance. Ignition delay is composed of physical and chemical delay; physical delay accounts for heating, atomization, vaporization and mixing time after injection [1], whereas chemical delay is purely attributed to chemical reactions. This study focuses on the examination and evaluation of the chemical delay. Two purposefully designed and built experimental devices are used for the study; a rapid compression machine (RCM) and a shock tube. RCMs and shock tubes have been widely used for fuel reactivity studies [2-4]. A shock tube allows for measurements at relatively high temperature, where short IDTs are observed. RCMs, on the other hand, cover a lower temperature regime than a shock tube, but have advantages of measuring longer IDTs. In terms of ignition delay studies, there are three specific temperature regimes which have their own distinctive chemical pathways.

2   Experimental Methods

2.1 Testing Fuels

F-24 aviation fuel has been selected to represent conventional kerosene fuels. The composition of F-24 is comparable to JP-8 military aviation fuel and is created from conventional Jet-A with the addition of the JP-8 military-spec required additives. Conventional jet fuels contain a wide variety of hydrocarbon species as shown in Figure 1 first row. Alcohol to jet (ATJ) type alternative fuels are derived from biomass-derived alcohol (iso-butanol), and thus have a unique chemical composition. Two heavily branched alkanes, iso-dodecane(2,2,4,4,6 or 2,2,4,4,6 pentamethyl heptane) and iso-cetane(2,2,4,4,6,8,8 or 2,2,4,4,6,6,8 heptamethylnonane) are major species of the commercial sample ATJ fuel used in this study, comprising 78.3 and 16.3 weight % respectively, as shown in Figure 1 last row.   Due to its unique composition, ATJ has an extremely low DCN (<17.7), and is expected to show considerably low reactivity. Along with two neat fuels, F-24 and ATJ, their blends in

Figure 1 GC/MS of tested fuels and blends

different mixing ratios (20:80, 40:60, 60:40 and 80:20 in volume %) are examined. Properties of the blended fuels are listed in Table 1. By blending a representative jet fuel and an extremely low CN fuel, a wide range of CN (48.5 to 17.7) can be examined. Neat ATJ fuel has prominent peaks of iso-C_{12} and iso-C_{16} whereas F-24 has diverse hydrocarbon components from C_8 to C_{18}. Blend fuels have peaks from both neat fuels, and their normalized abundance (relative concentration) depends on blending ratio.
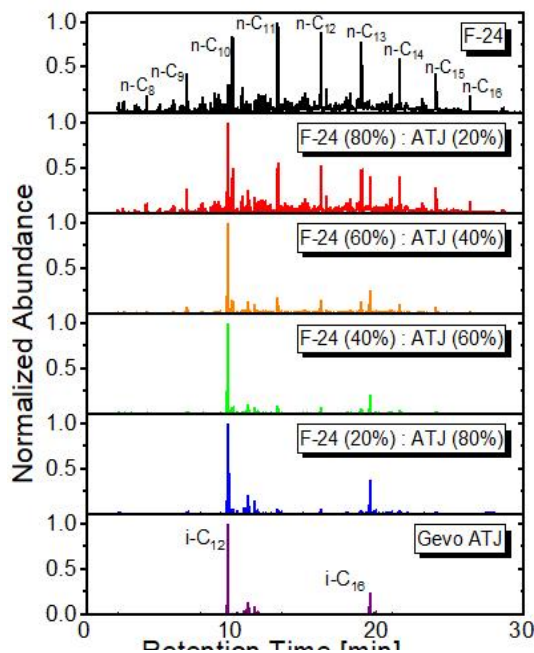
Table 1 : Physical / Chemical Properties of Fuels

| Fuel	[vol %]	**F-24**	**80/20**	**60/40**	**40/60**	**20/80**	**ATJ**
Properties	Methods	Properties					
Cetane Number	ASTM D613	48.5	42	35.5	29.4	<21.4[a]	<17.7[a,b]
MW [g/mol]	(calculated)	160.6	164.08	167.56	171.04	174.52	178
Density [g/ml]	ASTM D4052	0.804	0.795	0.7862	0.7774	0.7687	0.7595
HCR	SAE J1829	1.97	1.98	2.02	2.11	2.11	2.16
C contents [wt%]	ASTM D5291	85.84	85.67	85.43	84.94	84.92	84.63
H contents [wt%]	ASTM D5291	14.16	14.22	14.48	15.06	15.01	15.37

[a] Lowest cetane number which can be measured from ASTM D613 is 21.4
[b] DCN 17.7 is measured from ASTM D6890

2.2 Ignition Delay Time Measurements

Ignition delay times of fuels and blends are measured in both a shock tube and RCM at the University of Illinois at Urbana-Champaign. A shock tube is a device in which a driven gas is compressed by an incoming and reflected normal shock wave, caused by a driver gas, resulting in a rapid increase in pressure and temperature. The schematic of the device is shown in Figure 2a. The shock tube maintains an ID of 63.5mm throughout all sections, except for the diaphragm section which has a special square-to-round-transition design for proper normal shock development. The driver, diaphragm and driven sections are 2743mm, 203.2mm, and 4227mm, respectively. Driven and diaphragm sections can be heated to a temperature at which most of the fuels can be fully vaporized and fully premixed, 125ºC

throughout the study. Frozen Shock Wave Calculator (FROSH) code, written by Hanson *et al* . [5], is used to calculate incident and reflected shock conditions. Incident and reflected shock speed are measured from five equally spaced shock counters (PCB 111A22 pressure transducers), and pressure trace history is measured 25.4mm from end wall through a Kistler 6031B pressure transducer. A tailored He and N_2 mixture is used as driven gas. A premixed fuel, oxidizer and diluent gas (79% N_2 and 21% O_2) mixture is prepared in external mixing vessel and fed into driven section through heated and insulated tubing at the designated pressure. The pressure of reflected shock condition slightly varies from the targeted pressure over repeated tests. As the rate of oxidation increases with pressure [6], IDTs are expected to have negative power-law dependency, $\tau \sim P^N$. Previous studies have shown N corresponds to -1 at performed temperature and pressure conditions in this study [7-12]. The RCM is a pneumatically driven, hydraulically stopped device that emulates a single compression stroke found in reciprocating engines. Details on specifications of the device and testing procedure can be found in Figure 2b, and author's former studies[4, 13, 14]. The temperature (T) and pressure (P) of compressed conditions are calculated post experiment under adiabatic core assumption, following the relation: $\int_{T_0}^{T_c} \frac{\gamma}{\gamma-1} \frac{dT}{T} = ln \frac{p_c}{p_0}$ [15], where γ is the temperature-dependent specific heat ratio, and the subscripts 0 and *c* correspond to initial and compressed condition. For both devices, IDTs are evaluated from the pressure trace history. The onset of ignition in this study is designated as the moment of maximum pressure rise. The IDT is the time duration between the onset of ignition and the moment when the premixed mixture reaches the autoignition condition; Top dead center (TDC), or end of compression (EOC) in RCM, and the reflected shock condition in shock tube. When multi stage ignition is observed, mostly two stages, overall delay time(τ) can be divided into first(τ_1)and second stage ignition delay time (τ_2), as shown in Figure 2c.
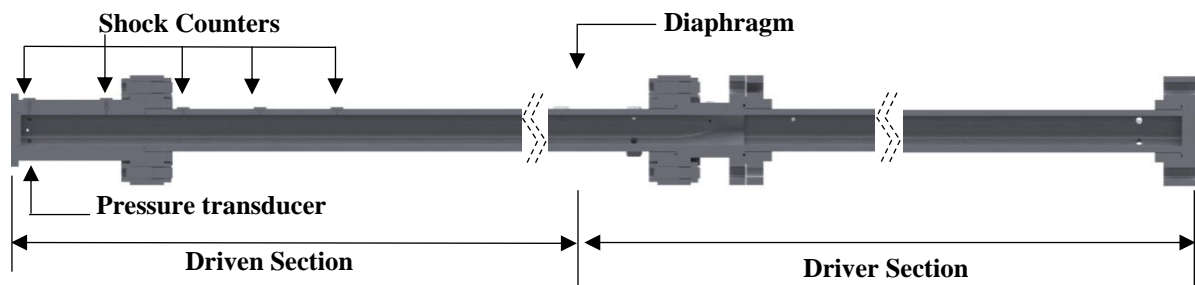
a. Schematics of shock tube
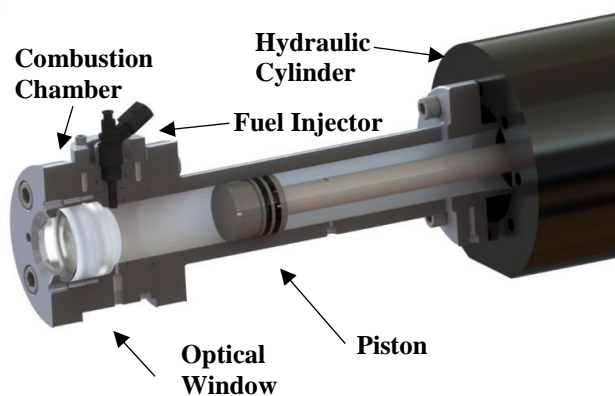
b. Schematics of RCM DTC configuration [17]
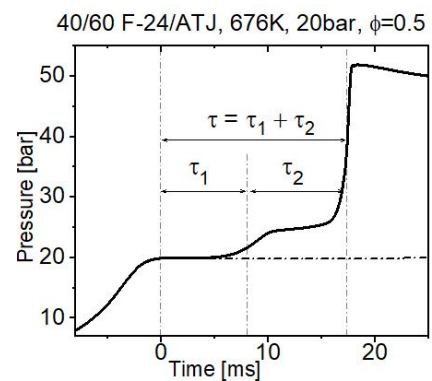
c. Example of two stage ignition

Figure 2 Schematic of shock tube and RCM pressure trace example
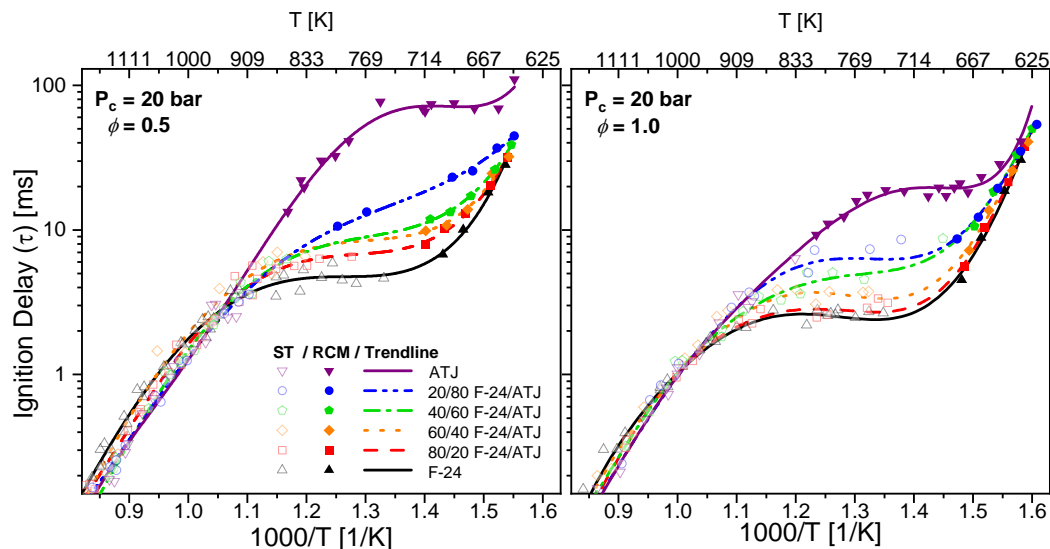
3   Results and Discussion

Figure 3 Shock tube and RCM ignition delay time integration

Ignition delay times of neat fuels and their blends at low to high temperature conditions are extensively measured in the RCM and Shock Tube, as shown in Figure 3. As expected, extremely long IDTs of neat ATJ are observed due to its unique chemical compositions. Heavily branched alkanes, isocetane and isododecane, are known to have retarded ignition delay [16, 17]. Compared to normal alkanes, branched alkanes lack secondary C-H bonds, inhibiting favorable six-membered ring transitions during $RO_2 \leftrightarrow QOOH$ isomerization [18]. This isomerization reaction is known to govern the reaction rate of the low temperature pathway [18, 19]. Retarded isomerization slows down the overall chain branching pathways, resulting in extremely low autoignition reactivity.
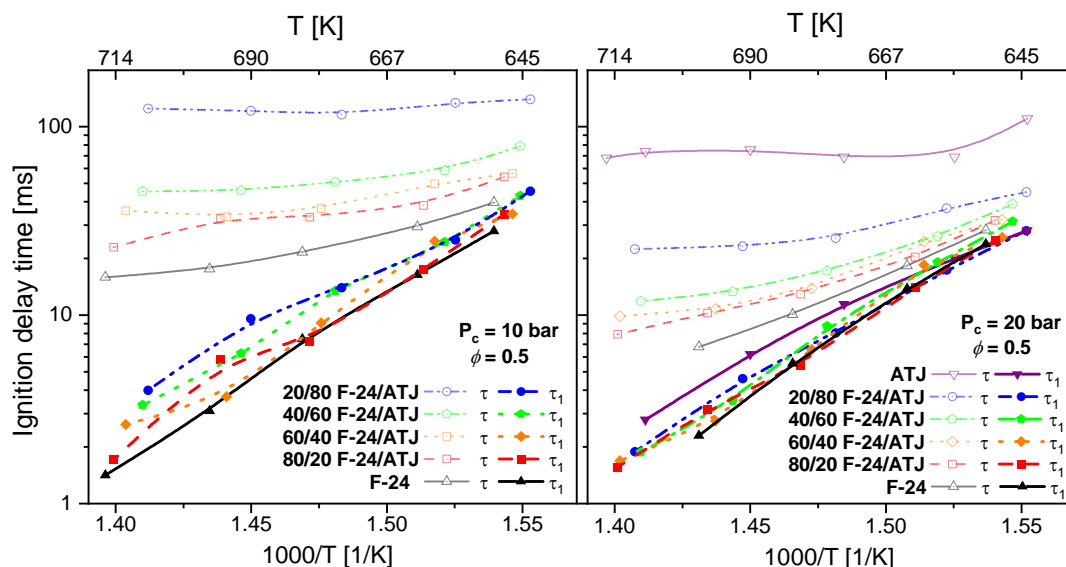

Figure 4 First stage ignition delay time measured in RCM

Stoichiometric conditions have shorter IDT compared to lean conditions, due to increased heat release during RO_2 formation expediting the reaction rate of accompanied radical chain branching pathways [14]. Negative pressure dependencies are also observed among different pressure conditions. Deviation among the fuels tends to be greater with longer IDT; lean and low-pressure conditions. These general tendencies correspond with the author's pervious works [13, 14, 18, 20].

Reactivity generally decreases with CN of the fuels, however, at lower temperature, the variation of reactivity decreases. Comparing six figures at a glance, IDT variation among the fuels is more observable when the slopes of Arrhenius plots start to curve, entering to the NTC regime. For example, at $P_c = 30$ bar, stoichiometric condition, blended fuels and neat F-24 show similar autoignition behavior. Neat ATJ fuel also shows similar behavior at the two lowest conditions but starts to deviate from other fuels when entering into NTC behavior. At $P_c = 10$ bar, $\phi = 0.5$, the longest IDT conditions, the difference in IDT among the fuels is much more prominent than other conditions as all the fuels exhibit apparent NTC behavior. Two stage ignition behavior tends to be more observable when fuels exhibit NTC behavior. Separated first stage IDT under two example conditions ($P_c = 10$ bar, $\phi = 0.5$ and $P_c = 20$ bar, $\phi = 0.5$) which exhibit clear two stage ignition behavior are shown in Figure 4. Compared to τ (faded symbols and lines), τ_1 deviations among the fuels are minor. Neat F-24 and blends exhibit very similar τ_1. Discrepancies of τ_1 between neat ATJ and other fuels are smaller compared to differences in τ. The pressure contribution to τ_1 is much smaller than overall τ. These two aspects, relatively fuel and pressure insensitive τ_1 at low temperature, agrees with a former experimental study [13] that states CN and τ_1 are less sensitive than overall τ. At low temperature conditions, H abstraction from the fuel components initiates the first stage reaction [21]. Activation energy of H abstraction from alkane species decreases with length of chain, and increases with branching, but varies in a small range [22, 23]. Similarity in activation energy accounts for τ_1 insensitivity to the chemical composition of fuels. Several studies observed NTC behavior of first stage reaction in shock tube experiments [24] or chemical simulations [21, 25], but the measurement temperature conditions of the RCM in this study are not high enough to see NTC behavior of τ_1. Considering small differences in τ_1 among the fuels, reaction steps after the H abstraction are account for deviation of overall τ. Radical chain branching reaction, $R\cdot + O_2 \leftrightarrow RO_2 \leftrightarrow QOOH (+O_2) \leftrightarrow OOQOOH \rightarrow 2OH + products$, controls low temperature reactivity of autoignition [19]. Formation of RO_2 from alky oxidation is known to be a major heat release source during first stage reactions [26]. The nature of the exothermic reaction shifts equilibrium back when the surrounding temperature is higher [27], slowing down the first stage reaction. The subsequent $RO_2 \leftrightarrow QOOH$ isomerization reaction is quite endothermic, known to be major limiting step of the first stage reaction, occurring during τ_2 [14]. Accounting that τ_1 is insensitive to species, the type of species 'R' during the NTC behavior determines overall ignition delay of the fuels. Retarded $RO_2 \leftrightarrow QOOH$ isomerization of branched alkanes in ATJ cause more prominent NTC behavior compared to F-24. As temperature increases, NTC behavior deviates IDT of ATJ from other blends more, until governing reactions associate with high temperature pathways. Reactivities of blends tend to be more favorable to F-24 influences. RO_2 isomerization of heavily branched species comprising neat ATJ is retarded, and equilibrium of former step shifts back to reactants. $R\cdot + O_2 \leftrightarrow RO_2$ competes with the $R\cdot + O_2 \rightarrow HO_2 \leftrightarrow$ alkene pathway. The formation of HO_2 radicals rather than chain branching pathways (producing OH) slows down the reactivity and reveal prominent NTC behavior. In other words, the addition of F-24, even in a small portion (20%), shifts the overall reaction pathways to chain branching favorable pathways, and expedites reaction rates.

At high temperature, above around 900K, most of the fuels and blends are showing similar, short, and linear IDTs. Pyrolysis of the fuel components initiate the reaction at high temperature. Pyrolysis of neat F-24 is similar to other conventional jet fuels such as Jet A. Hydrocarbon species decompose to small species such as CH_4, C_2H_4, C_3H_6, 1-butene, benzene and toluene [28]. Major products of ATJ pyrolysis also include CH_4, C_2H_4, C_3H_6, but slightly larger and more reactive species such as C_2H_6, C_2H_2, a-C_3H_4, p-C_3H_4 and i-C_4H_8 are also produced [29]. These species lead to faster reactions compared to F-24 above 950K where reactions initiate from pyrolysis.

By conducting extensive testing of autoignition behavior, obtained data and findings are conducive to generally understand reactivity of jet fuels across a wide range of cetane number. Temperature and pressure conditions tested span regions applicable to practical engines and can help inform the design and development of next generation engines which are less sensitive to fuel property variations.

References

[1] Assanis, D. N., Filipi, Z. S., Fiveland, S. B., and Syrimis, M. (2003). A Predictive Ignition Delay Correlation Under Steady-State and Transient Operation of a Direct Injection Diesel Engine. Journal of Engineering for Gas Turbines and Power. 125: 450-457

[2] Westbrook, C. K., Curran, H. J., et al. (1998). The effects of pressure, temperature, and concentration on the reactivity of alkanes: Experiments and modeling in a rapid compression machine. Proc. Combust. Inst. . 27: 371

[3] Minetti, R., Carlier, M., et al. (1995). A rapid compression machine investigation of oxidation and auto-ignition of n-Heptane: Measurements and modeling. Combustion and Flame. 102: 298

[4] Allen, C., Toulson, E., Edwards, T., and Lee, T. (2012). Application of a Novel Charge Preparation Approach to Testing the Autoignition Characteristics of JP-8 and Camelina Hydroprocessed Renewable Jet Fuel in a Rapid Compression Machine. Combustion and Flame. 159: 2780-2788

[5] Peterson, E. L., "A Shock Tube and Diagnostics for Chemistry Measurements at Elevated Pressures with Application to Methane Ignition", in Mechanical Engineering. 1998, Stanford Uinversity.

[6] Smith, J. M., Simmie, J. M. and Curran, H. J. (2005). Autoignition of heptanes; experiments and modeling. International Journal of Chemical Kinetics. 37: 728-736

[7] Kumar, K. and Sung, C.-J. (2010). A comparative experimental study of the autoignition characteristics of alternative and conventional jet fuel/oxidizer mixtures. Fuel. 89: 2853-2863

[8] Kumar, K. and Sung, C. J. (2010). An experimental study of the autoignition characteristics of conventional jet fuel/oxidizer mixtures: Jet-A and JP-8. Combustion and Flame. 157: 676-685

[9] Vasu, S. S., Davidson, D. F. and Hanson, R. K. (2008). Jet fuel ignition delay times: Shock tube experiments over wide conditions and surrogate model predictions. Combustion and Flame. 152: 125-143

[10] Oehlschlaeger, M. A., Shen, H.-P. S., Steinberg, J., and Vanderover, J., "The Ignition of C7 and C16 Normal and Branched Alkanes at Elevated Pressures", in Proceedings of the 6th U.S. National Combustion Meeting. 2010.

[11] Valco, D., Gentz, G., et al. (2014). Autoignition behavior of synthetic alternative jet fuels: An examination of chemical composition effects on ignition delays at low to intermediate temperatures. Proceedings of the Combustion Institute.

[12] Shen, H.-P. S., Steinberg, J., Vanderover, J., and Oehlschlaeger, M. A. (2009). A Shock Tube Study of the Ignition of n-Heptane, n-Decane, n-Dodecane, and n-Tetradecane at Elevated Pressures. Energy & Fuels. 23: 2482-2489

[13] Min, K., Valco, D. J., et al. (2019). Autoignition of varied cetane number fuels at low temperatures. Proceedings of the Combustion Institute. 37: 5003-5011

[14] Kyungwook Min, D. V., Anna Oldani, Tim Edwards, Tonghun Lee. (2017). Autoignition Behavior of Jet Fuel Relevant Pure Hydrocarbon Components in a Rapid Compression Machine. Proceedings of 10th U. S. National Combustion Meeting. 1: 2579

[15] Mittal, G., "A rapid compression machine - design, characterization, and autoignition investigations", in Department of Mechanical and Aerospace Engineering. 2006, Case Western Reserve University: Cleveland, OH. p. 179.

[16] Mathes, A., Ries, J., et al., "Binary Mixtures of Branched and Aromatic Pure Component Fuels as Surrogates for Future Diesel Fuels". 2010, SAE International.

[17] Oehlschlaeger, M. A., Steinberg, J., Westbrook, C. K., and Pitz, W. J. (2009). The autoignition of iso-cetane at high to moderate temperatures and elevated pressures: Shock tube experiments and kinetic modeling. Combustion and Flame. 156: 2165-2172

[18] Valco, D. J., Min, K., et al. (2017). Low temperature autoignition of conventional jet fuels and surrogate jet fuels with targeted properties in a rapid compression machine. Proceedings of the Combustion Institute. 36: 3687-3694

[19] Battin-Leclerc, F. (2008). Detailed chemical kinetic models for the low-temperature combustion of hydrocarbons with application to gasoline and diesel fuel surrogates. Progress in Energy and Combustion Science. 34: 440

[20] Kyungwook Min, D. V., Anna Oldani, Tim Edwards, Tonghun Lee. (2015). An ignition delay study of category c alternative aviation fuel. ASME 2015 International Mechanical Engineering Congress & Exposition.

[21] Zhao, P. and Law, C. K. (2013). The role of global and detailed kinetics in the first-stage ignition delay in NTC-affected phenomena. Combustion and Flame. 160: 2352-2358

[22] Zboray, M., Bell, A. T. and Iglesia, E. (2009). Role of C−H Bond Strength in the Rate and Selectivity of Oxidative Dehydrogenation of Alkanes. The Journal of Physical Chemistry C. 113: 12380-12386

[23] Ma, X. and Schobert, H. H. (2003). Estimating the Activation Energy of Hydrogen-Abstraction Reactions Involving Hydrocarbons by Thermochemical Properties. Industrial & Engineering Chemistry Research. 42: 1151-1161

[24] Campbell, M. F., Wang, S., et al. (2015). Constrained reaction volume shock tube study of n-heptane oxidation: Ignition delay times and time-histories of multiple species and temperature. Proceedings of the Combustion Institute. 35: 231-239

[25] Zhang, P., Ji, W., et al. (2016). First-stage ignition delay in the negative temperature coefficient behavior: Experiment and simulation. Combustion and Flame. 167: 14-23

[26] Law, C. K. and Zhao, P. (2012). NTC-affected ignition in nonpremixed counterflow. Combustion and Flame. 159: 1044-1054

[27] Griffiths, J. F., Halford-Maw, P. A. and Rose, D. J. (1993). Fundamental features of hydrocarbon autoignition in a rapid compression machine. Combustion and Flame. 95: 291

[28] Han, X., Liszka, M., et al. (2019). A high pressure shock tube study of pyrolysis of real jet fuel Jet A. Proceedings of the Combustion Institute. 37: 189-196

[29] Guzman, J., Kukkadapu, G., Brezinsky, K., and Westbrook, C. (2019). Experimental and modeling study of the pyrolysis and oxidation of an iso-paraffinic alcohol-to-jet fuel. Combustion and Flame. 201: 57-64