Auto-Ignition Characteristics Study of Gas-to-Liquid Fuel at High Pressures and Low Temperatures

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The need for finding an alternative to oil-based transportation fuels is greater now than ever before due to environmental impact and supply security. Alternative fuels obtained from feedstocks such as biomass, natural gas, and coal are called synthetic paraffinic kerosene (SPK) fuels. Recently, the interest on SPK fuels as a viable alternative fuel for aviation transportation is enormous as they do not warrant any major modifications to the existing fuel injection/combustor system. Furthermore, the SPK fuels obtained through F–T synthesis are preferred as the fuel composition can be appropriately tailored for specific applications. Among SPK fuels, GTL fuel is preferred over conventional jet fuels due to cleaner combustion characteristics as a result of less aromatic content and the near absence of sulfur. [1]. The GTL fuel can also be surrogate for gasoline, diesel, and aviation fuels [2]. Over the years, the potential for deriving high value products from natural gas [3–5] and its abundant availability have attracted the pioneers in GTL production technology, such as Syntroleum, Shell, Sasol, and Chevron, to build small- and medium-scale GTL plants across the globe. The availability of the world’s third largest natural gas reserve in Qatar (with proven reserves of about $90 \times 10^{12} \text{cu ft}$ [6]) has led to the construction of world’s largest GTL plant, Pearl GTL, jointly by Qatar-Petroleum and Shell at a cost of about $18 billion. This has enabled Qatar airways to attempt a commercial flight from London, UK to Doha, Qatar, using a 50–50% blend of GTL fuel and conventional Jet A-1 fuel [7].

The SPK fuels produced using F–T process are mainly composed of normal alkanes, iso-alkanes, and cyclic alkanes, which are substantially different from those of conventional jet fuels such as Jet A, Jet A-1, and JP-8. Synthetic fuels have a very small concentration of cycloalkanes in comparing with conventional jet fuels, and this small number varies based on the different production processes and companies. Moses [8] has done a very good comparison between different available synthetic fuels. He showed that among SPK fuels, Syntroleum aviation fuel provided by AFRL, designated with S-8, has almost no cycloalkanes. The difference in fuel chemical properties will have a significant influence on the combustion and emission characteristics in combustors. Therefore, a complete knowledge of fundamental combustion parameters for GTL fuel at combustor conditions is essential in order to improve and optimize the combustor design and engine efficiency. Furthermore, these fundamental combustion parameters are necessary to develop, validate, and to improve the prediction capabilities of computational tools and chemical kinetics models. Among these fundamental combustion
parameters, the investigation of the onset of auto-ignition [9,10] for GTL fuel is extremely relevant and necessary for the combustion community, particularly for gas turbine and internal combustion engines in the transportation industry [11,12].

The onset of auto-ignition is the set of thermodynamic conditions at which the combustion process occurs spontaneously and simultaneously throughout the combustion chamber [13]. For a particular mixture of fuel, oxidizer, and diluent, the temperature and the pressure are the key parameters to consider as the drivers to auto-ignition [14]. Time is also a factor in driving auto-ignition. A parameter called ignition delay time can be experimentally determined as the time a mixture may remain at a temperature and pressure before auto-ignition occurs [15]. Typically, rapid compression machines or shock tubes are used to determine the ignition delay times of a mixture. The results from such experiments, even though widely accepted, do not represent the conditions typically found in practical applications of combustion system where the pressure and temperature are constantly changing due to flame propagation. Using the experimentally developed facility in this study, a controlled combustion event in spherical constant volume combustion chamber produces an increase in the pressure and temperature of the unburned mixture [16]. When auto-ignition conditions are reached, the unburned gas instantly ignites and produces a series of pressure waves that can be detected by the pressure transducer. The conditions of the unburned gas that initiate the pressure waves are the conditions at which auto-ignition occurs and are more representative of the varying conditions typically found in a combustion system such as internal combustion engines.

Kumar and Sung [17] have done an experimental study of auto-ignition characteristics of GTL and conventional fuel/air mixtures and observed two-stage ignition delay response. Their further study on laminar burning speed indicated that S-8 GTL produces a robust flame compared to Jet-A [18]. Wang and Oehlschlager [19] have investigated the ignition behavior of several conventional and GTL fuels using a heated shock tube. Their ignition delay time measurements were almost the same for GTL and Jet-A at temperatures higher than 1000 K. However, at lower temperatures significant differences were observed between those of GTL and Jet-A fuels. In order to simulate the combustion behavior of GTL fuel, many groups tried to find a surrogate mixture for GTL fuels. Huber et al. [20] provided surrogates for GTL fuel based on the thermophysical properties incorporating with volatility data. Naik et al. [21] developed a three-component, iso-octane, n-decane, and n-dodecane, chemical kinetics model as a surrogate for GTL fuel and compared the predictions with the experimental results reported by Ji et al. [22]. The comparison showed that the model was able to accurately predict the laminar burning speeds of GTL fuels, but can only be used for ignition delay time calculation at high temperatures. Dooley et al. [23] also developed a chemical kinetic model based on the mixtures of iso-octane and n-dodecane to mimic the combustion behavior of GTL fuels. The predictions of auto-ignition, extinction limits, and species concentration profile were reported to agree well with the experimental data. The ignition behaviors have been evaluated using different experimental configurations such as counterflow burner [24], rapid compression machine [17], and shock tubes [19]. The outcome of these studies highlighted the fact that GTL fuel had a much larger resistance to flame stretch effects and robust combustion behavior when compared to conventional jet fuels. The more notable combustion behavior was the shorter ignition delay of GTL fuel than the conventional counterparts. However, it is important to note that all of the above studies have been carried out either at atmospheric pressure or at discrete intermediate pressures. The data for the onset of auto-ignition for GTL fuel have not comprehensively been measured in the conditions which are identical to internal combustion engines.

In this study, the onset of auto-ignition for GTL fuel/air mixtures has been measured for different equivalence ratios of 0.8–1.2 and different initial pressures of 8.6, 10, and 12 atm at an initial temperature of 450 K. The GTL fuel used in this research was supplied by AFRL, designated by Synthroleum S-8, which was derived from natural gas via F–T process. The experiments have been done in a high pressure and temperature spherical chamber, and the pressure rise has been collected using high-speed pressure transducer and data acquisition systems. Critical pressures and temperatures the combustion mixture at which auto-ignition takes place have been identified by detecting aggressive oscillation of pressure data during the spontaneous combustion process throughout the unburned gas mixture. Several detailed chemical kinetics mechanisms have been compared and used to study the onset of auto-ignition conditions. A blend of 32% iso-octane, 25% n-decane, and 43% n-dodecane [21] was employed as the surrogate of GTL fuel for chemical kinetics study and filling process.

Experimental Setup

The core component of the experimental setup includes a spherical combustion chamber that enables the measurement of the pressure rise during flame propagation. The spherical chamber is designed to withstand pressures up to 400 atm and is located in an oven which can be heated up to 500 K. It includes three ionization probes to check the symmetry of the spherical flame. A Kistler 601CA high-temperature pressure transducer in conjunction with a Kistler 5010B charge amplifier is used to record the dynamic pressure rise during the combustion process. The chamber is also equipped with two extended spark plugs for ignition at the center of chamber and a K-type thermocouple to measure the mixture gas temperature. The gas supply manifold, mainly constructed of 304 and 316 stainless steel Swagelok fittings and tubing, is predisposed to accommodate inputs from five simultaneous gas cylinders, thus allowing for an inventory of gas mixtures to be always readily available for immediate use. Two vacuum pumps help evacuate the system faster and allow for independent testing of the two chambers. The temperature controllers are proportionally programmable with redundant safety feature for temperature protection and electric shock.

Another key element of the apparatus is the liquid filling system where liquid fuel is allowed to enter and evaporate in a temperature-controlled portion of the manifold. A high-pressure transducer closely coupled to this section of the manifold is used to monitor the partial pressure of the vaporized fuel, and hence control the amount of fuel that will be used in the experiment. A GC system in conjunction with the specialized heated lines to prevent condensation was used to check the composition of premixed fuel/air mixture inside the chamber to verify the filling process based on partial pressure method. The configuration of experimental facilities and their connections are shown in Fig. 1. All data acquisition and analysis were done by several dedicated PCs using a high-speed DAQ card and isolated input and output modules for temperature, voltages, and pressure measurements as well as automatic delayed firing via control of the high-voltage coil driving the spark plugs. The raw pressure signal produced by the high-speed pressure transducer contains digitization noise resulting from data acquisition system process of converting a voltage signal to a digital value. The digitization noise is approximately 0.25 psi/bit, which is certainly negligible for the range of pressure measurements of interest. For any set of data to be deemed acceptable, three consecutive experimental runs have to yield the exact pressure curve to ensure that the confidence level of the experiments is above 95% [25]. More information about the experimental setup can be found in previous publication [3,4,16,26–35].

Results and Discussion

As previously discussed, synthetic fuels produced by the F–T method have become increasingly popular as substitutes to the conventional hydrocarbon fuels such as diesel, gasoline, and jet fuels [36]. The GTL fuel used in this study was provided by the
AFRL [8,37]. This fuel was produced in the U.S. from natural gas through an F–T process called low-temperature cobalt catalyst [8] in a small pilot plant by Syntroleum in Oklahoma. The specification properties of this fuel are presented in Table 1. It can be seen that the percentage of aromatic (cyclic) is zero. A blend of 32% iso-octane, 25% n-decane, and 43% n-dodecane [21] was employed as the surrogates of GTL fuel for chemical kinetics study and filling process. The initial mixture composition for GTL/air mixture is defined as

\[
\phi \left( 0.32 \ C_8H_{18} + 0.25 \ C_{10}H_{22} + 0.43 \ C_{12}H_{26} \right) \\
+ 15.83 \left( O_2 + 3.76N_2 \right)
\]  

(1)

This surrogate mixture has an empirical formula of $C_{10.22}H_{22.44}$, an estimated cetane number of 61, and a molar mass of 145.37 g/mol.

In this study, the propensity of GTL/air mixture to auto-ignite and the conditions that produce the onset of auto-ignition were measured and analyzed for various equivalence ratios and initial conditions. Measurements for the onset of auto-ignition of GTL/air mixture have been recorded in the spherical chamber for different equivalence ratios of 0.8–1.2 and different initial pressures of 8.6, 10, and 12 atm at initial temperature of 450 K. During the compression of unburned mixture due to flame propagation, which acts as a piston, both temperature and pressure of the unburned gas increase. At a specific condition, auto-ignition of all of the unburned gases occurs. The temperature and pressure that instantaneously produce auto-ignition are measured and reported as the onset of auto-ignition. To detect the onset of auto-ignition, the derivative of the measured pressure ($dp/dt$) was evaluated and used as a nonsubjective method to determine the auto-ignition pressure. The measured pressure signal begins to oscillate once auto-ignition occurs due to the shock waves bouncing around in the combustion chamber. The derivative with respect to time of the pressure signal will oscillate very aggressively between positive and negative values once auto-ignition occurs, thus providing a convenient method to detect the onset of auto-ignition. It was assumed that unburned gas is compressed isentropically up to the onset of auto-ignition, and the temperature at the onset of auto-ignition was determined using isentropic relation of compression.

Figure 2 shows the pressure–time traces of combustion of GTL/air mixture for four initial pressures of 2, 8.6, 10, and 12 atm at initial temperature of 450 K and equivalence ratio of 0.8. For the case of initial pressure of 2 atm, no auto-ignition was observed, normal combustion process occurred, and the pressure curve is very smooth as shown by the solid line in Fig. 2. At the onset of auto-ignition, a sudden oscillation in the pressure is detected as shown by points A, B, and C in Fig. 2 for initial pressures of 8.6, 10, and 12, respectively, along with audible noise as a good

### Table 1 Specification properties of Syntroleum S-8 fuel

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flash point (°C)</td>
<td>48</td>
</tr>
<tr>
<td>Freezing point (°C)</td>
<td>-51</td>
</tr>
<tr>
<td>Density at 15 °C (kg/L)</td>
<td>0.756</td>
</tr>
<tr>
<td>Viscosity at –20 °C (mm²/s)</td>
<td>4.3</td>
</tr>
<tr>
<td>Net heat of combustion (MJ/kg)</td>
<td>44.1</td>
</tr>
<tr>
<td>Conductivity (pS/m)</td>
<td>128</td>
</tr>
<tr>
<td>Lubricity test (BOCLE) wear scar (mm)</td>
<td>0.59</td>
</tr>
<tr>
<td>Aromatics (% vol)</td>
<td>0.0</td>
</tr>
<tr>
<td>Total sulfur (% mass)</td>
<td>&lt;0.0003</td>
</tr>
<tr>
<td>Hydrogen content (% mass)</td>
<td>15.4</td>
</tr>
</tbody>
</table>
indication that unburned mixture was auto-ignited. The auto-ignition pressure traces shown in Fig. 2 are very similar to those in internal combustion engines reported by Heywood [38]. The auto-ignition pressures were accurately determined using pressure derivative technique and locating the point at which the pressure derivative with respect to time becomes discontinuous as shown in Fig. 3. It can be observed visually in this figure that the oscillatory pressure waves caused by auto-ignition are easily detected by this technique. As it was mentioned, the corresponding auto-ignition temperatures of unburned gas were measured assuming that the unburned gas mixture was compressed isentropically.

While development of the chemical kinetics mechanism of GTL fuel is in its initial stage, there are several mechanisms that can predict GTL combustion characteristics such as laminar burning speed and ignition delay time [21,23,39,40]. These mechanisms are summarized in Table 2. As shown in the table, in terms of computational time which is proportional to number of species and reactions, Dooley et al. mechanism [23] is the most expensive mechanism due to the larger number of species, and Yu et al. mechanism [40] is the least expensive mechanism. All three surrogates of iso-octane, n-decane, and n-dodecane are included in Naik et al. [21], Dooley et al. [23], and Ranzi et al. [39] mechanisms except Yu et al. mechanism [40] which only has two surrogates of 2,5-dimethylhexane (one of the octane’s isomers) and n-dodecane. The above proposed composition of 32% iso-octane, 25% n-decane, and 43% n-dodecane is applicable for the first three mechanisms in Table 2. For Yu et al. mechanism [40], its own suggested composition of 41.9% 2,5-dimethylhexane and 58.1% n-dodecane has been used.

The ignition delay time computations were performed with assumption of constant volume/constant internal energy using CANTERA solver [41]. The ignition delay time was calculated when the temperature reached a value of 400 K above the initial temperature. Figure 4 shows a comparison of ignition delay times between available kinetics mechanisms of GTL fuel with the heated shock tube experimental data of Wang and Oehlschlager [19] at equivalence ratio of 1 and pressure of 20 atm for a wide range of temperatures. As it can be seen, Ranzi et al. [39] and Yu et al. [40] mechanisms have a good agreement with the experimental results for both low and high temperatures. Since the agreement of Ranzi et al. [39] mechanism with experimental data at intermediate temperatures is slightly better than those predicted by Yu et al. [40] and also it includes all three surrogates of iso-octane, n-decane, and n-dodecane, it was used in this study.

![Fig. 3 Comparison of pressure rate–time traces of auto-ignition of GTL/air mixture for three different initial pressures of 8.6, 10, and 12 atm, at initial temperature of 450 K and equivalence ratio of 0.8.](image1)

![Fig. 4 Comparison of available GTL detailed kinetics mechanisms [21,23,39,40] with the experimental data [19] at equivalence ratio of 1 and pressure of 20 atm for a wide range of temperatures.](image2)

![Fig. 5 Theoretical ignition delay time for a wide range of pressures and temperatures using Ranzi et al. [39] mechanism for stoichiometric GTL/air mixture.](image3)

### Table 2 Comparison of different chemical kinetics mechanisms for GTL fuel

<table>
<thead>
<tr>
<th>Mechanism name</th>
<th>Number of species</th>
<th>Number of reactions</th>
<th>Available GTL surrogates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naik et al. [21]</td>
<td>753</td>
<td>7007</td>
<td>Iso-octane, n-decane, and n-dodecane</td>
</tr>
<tr>
<td>Dooley et al. [23]</td>
<td>3164</td>
<td>21,671</td>
<td>Iso-octane, n-decane, and n-dodecane</td>
</tr>
<tr>
<td>Ranzi et al. [39]</td>
<td>484</td>
<td>19,341</td>
<td>Iso-octane, n-decane, and n-dodecane</td>
</tr>
<tr>
<td>Yu et al. [40]</td>
<td>373</td>
<td>2037</td>
<td>2,5-dimethylhexane and n-dodecane</td>
</tr>
</tbody>
</table>

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As shown in Fig. 5, at low-temperature conditions \((T < 800 \text{ K})\), both temperature and pressure have a negative dependency on ignition delay time. It can be seen that for low-temperature and high-pressure conditions indicated by dashed rectangular box, as either temperature or pressure increases, the ignition delay time decreases or in other words, the propensity of auto-ignition increases. Figure 5 also shows that pressure has a minor effect on ignition delay time for low temperatures, and the effect of pressure on ignition delay time increases as the temperature increases. It can be concluded from this figure that for low-temperature conditions, the ignition delay time is a strong function of temperature.

The experimental critical temperatures and pressures in this work at the onset of auto-ignition along with theoretical ignition delay time using Ranzi et al. \cite{39} mechanism for GTL/air mixture at different equivalence ratios are shown in Fig. 6 and also listed in Table 3. In Fig. 6, as mixture pressure increases, the temperature at which auto-ignition occurs decreases for all three equivalence ratios. As shown in Fig. 7, increasing the temperature while the pressure is decreasing causes the ignition delay time to decrease. The ignition delay time tends to keep its negative dependency only with temperature. These experimental runs produced auto-ignition conditions at different pressures and only slightly different temperatures, indicating that the auto-ignition characteristics are a strong function of the temperature of the unburned gases.

Summary and Conclusions

In this paper, the onset of auto-ignition of GTL fuel was measured for a wide range of equivalence ratios from 0.8 to 1.2 and initial pressures of 8.6, 10, and 12 atm at initial temperature of 450 K using aggressive oscillation of pressure data during the spontaneous combustion process throughout the unburned mixture. The experiments were done in a high-pressure and temperature spherical chamber, and the pressure rise due to combustion was collected using high-speed pressure transducer and data acquisition systems. Several detailed kinetics mechanisms have been compared for ignition delay time calculations, and it was found that Ranzi et al. mechanism \cite{39} has a better agreement with the available experimental results in the literature. It was shown that at low unburned gas temperatures, both temperature and pressure have a negative dependency on the ignition delay time, and the auto-ignition characteristics are also a strong function of the unburned gas temperature.

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References
