Theoretical Prediction of Laminar Burning Speed and Ignition Delay Time of Gas-to-Liquid Fuel

Gas-to-liquid (GTL), an alternative synthetic jet fuel derived from natural gas through Fischer–Tropsch (F–T) process, has gained significant attention due to its cleaner combustion characteristics when compared to conventional counterparts. The effect of chemical composition on key performance aspects such as ignition delay, laminar burning speed, and emission characteristics has been experimentally studied. However, the development of chemical mechanism to predict those parameters for GTL fuel is still in its early stage. The GTL aviation fuel from Syntroleum Corporation, S-8, is used in this study. For theoretical predictions, a mixture of 32% iso-octane, 25% n-decane, and 43% n-dodecane by volume is considered as the surrogate for S-8 fuel. In this work, a detailed kinetics model (DKM) has been developed based on the chemical mechanisms reported for the GTL fuel. The DKM is employed in a constant internal energy and constant volume reactor to predict the ignition delay times for GTL over a wide range of temperatures, pressures, and equivalence ratios. The ignition delay times predicted using DKM are validated with those reported in the literature. Furthermore, the steady one-dimensional premixed flame code from CANTERA is used in conjunction with the chemical mechanisms to predict the laminar burning speeds for GTL fuel over a wide range of operating conditions. Comparison of ignition delay and laminar burning speed shows that the Ranzi et al. mechanism has a better agreement with the available experimental data, and therefore is used for further evaluation in this study. [DOI: 10.1115/1.4033984]

Keywords: ignition delay time, laminar burning speed, detailed kinetics model, chemical mechanism, gas-to-liquid, theoretical prediction, experimental data
compared the combustion characteristics of alternative jet fuels. The laminar flame speeds measured for conventional and alternative jet fuels were similar, although the ignition delay times of the latter were shorter than those of the former. Vukadinovic et al. [29] measured the laminar burning speed and Markstein number in a cubic vessel using the optical laser method. Ji et al. [30] investigated the laminar burning speed of jet fuel and its alternatives and found a 5–8% higher in laminar burning speed of synthetic and biofuels than standard jet fuel–air flames at elevated temperatures of the unburned mixtures. Singh et al. [31] measured the laminar flame speeds and Markstein lengths of n-decane, Jet-A, and S-8 and got similar laminar burning speed for equivalence ratio from 0.8 to 1.6.

In order to simulate the combustion behavior of GTL fuel, many groups tried to find a surrogate mixture for GTL fuels. Huber et al. [32] provided surrogates for GTL fuel based on the thermophysical properties incorporating with the volatility data. Naik et al. [33] came up with three-component surrogates (iso-octane, n-decane, and n-dodecane) for S-8 and Shell GTL fuels. They validated their chemical kinetic mechanism using the available experimental data from the literature. Dooley et al. [34] considered a mixture of iso-octane and n-dodecane as surrogates and validated their predictions with the experimental data reported by Wang and Oehlschlaeger [23]. Slavinskaya et al. [35] came up with another surrogate for GTL composed of n-decane, n-propylcyclohexane, and iso-octane. The chemical mechanism for the surrogates is validated by comparing the ignition delay time and laminar burning speed with the experimental data from the literature. Yu et al. [36] created a surrogate mixture of n-dodecane and 2,5-dimethylhexane (one of the octane’s isomers), and their predictions compared well with the experimental data from the literature. Dagaut et al. [37] investigated the mole fraction of the major species, ignition delay times, and the laminar burning speed of GTL fuel. They also studied the kinetics of oxidation of Shell GTL blended with hexanol both experimentally and theoretically [38]. Later, they compared the concentration profiles for the oxidation of GTL and Jet-A, and calculated the ignition delay times [39]. Zhu et al. [40] studied the ignition delay times for conventional jet fuels, alternative fuels (derived from natural gas and coal), and their blends using shock-tube/laser-absorption methods in various initial conditions. They observed similar trends of ignition delay time between the fuels with a small and evident difference in their activation energy.

Although there are some theoretical studies on the ignition delay time and laminar burning speed of GTL fuels, they are all done under certain temperatures, pressures, and equivalence ratios. A comprehensive study on the behavior of ignition delay time and laminar burning speed over a wide range of temperatures, pressures, and equivalence ratios has not been conducted yet. This serves as the motivation for the present study. The ignition delay time and laminar burning speed of GTL/air mixtures are predicted over a wide range of operating conditions. The GTL fuel from Syntroleum Corporation, S-8, is represented by a surrogate mixture in this study. The GTL fuel properties and its chemical composition are based on the reports from Air Force Research Laboratory (AFRL) [41,42]. In this work, a DKM has been developed based on the existing information on the chemical kinetics for the GTL jet fuel. The DKM predictions of ignition delay time and laminar burning speed are compared with those obtained using different chemical mechanisms [33,34,36,43] for the GTL fuel to highlight the predictive capabilities of different mechanisms with respect to the experimental data. The ignition delay time is calculated with the assumptions of constant volume and constant internal energy using the DKM [44]. For laminar burning speed prediction, the steady one-dimensional premixed flame code from CANTERA [45] has been used.

**DKM**

The most accurate way to determine the time-dependent behavior of the state of a reaction system is developing a DKM for the reacting system [44]. In this study, a constant internal energy and constant volume DKM is created to calculate the ignition delay time. In this model, the concentrations of all the species and the system temperature are time-dependent variables. This model consists of a full set of nonlinear ordinary differential equations for the prediction of species concentrations and temperature via species and energy balance equations, respectively. For a reaction system, any chemical reactions can be written as follows:

\[
\sum_{j=1}^{ns} \nu_{j}^{i} X_{j} \rightarrow \sum_{j=1}^{ns} \nu_{j}^{k} X_{j}, \quad k = 1, \ldots, nr
\]  

where \(X_{j}\) is the symbol of species \(j\), \(ns\) is the number of species, \(nr\) is the number of reactions, and \(\nu_{j}^{i}\) and \(\nu_{j}^{k}\) are the stoichiometric coefficients on the reactants and products side of the equation, respectively, for species \(j\) in the reaction \(i\). Then, the rate equation of species \(j\) can be expressed as

\[
\frac{d[X_{j}]}{dt} = \sum_{i=1}^{nr} \nu_{j}^{i} \dot{c}_{i}(T)
\]

\[\dot{c}_{i}(T) = k_{i} \prod_{j=1}^{ns} [X_{j}]^{\nu_{j}^{i}} - k_{r} \prod_{j=1}^{ns} [X_{j}]^{\nu_{r}^{i}}\]

where \(\prod_{j=1}^{ns} [X_{j}]^{\nu_{j}^{i}}\) is the net molar concentration rate of species \(j\), \(q_{i}\) is the rate-of-progress variable for the \(i\)th elementary reaction, and \(k_{i}\) and \(k_{r}\) are the elementary forward and reverse rate coefficients, respectively. For temperature, we need an additional rate equation which will be derived from energy balance

\[
\frac{dT}{dt} = \frac{-\sum_{j=1}^{ns} \dot{n}_{j} c_{v_{j}}(T)}{\sum_{j=1}^{ns} n_{j}}
\]

where \(\dot{n}_{j}\) is mole number of species \(j\), \(c_{v_{j}}(T)\) is the specific internal energy (per mole) of species \(j\) at temperature \(T\), and \(c_{v_{j}} = dc_{v}/dT\) is the specific heat at constant volume for species \(j\). Solving Eqs. (2) and (5) simultaneously can give us the concentrations and temperature profiles versus time, which describe the change of state of the system. The ignition delay time was calculated when the temperature reached a value of 400 K above the initial temperature.

The GTL fuel properties and its chemical composition have been provided by the AFRL [41,42]. This fuel was produced in the U.S. from natural gas through an F–T process called low-temperature cobalt catalyst [41] in small pilot plant by Syntroleum.

<table>
<thead>
<tr>
<th>Specification properties of Syntroleum S-8 fuel</th>
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<tbody>
<tr>
<td>Initial boiling point (K)</td>
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<tr>
<td>10% recovered (K)</td>
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<tr>
<td>20% recovered (K)</td>
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<tr>
<td>50% recovered (K)</td>
</tr>
<tr>
<td>90% recovered (K)</td>
</tr>
<tr>
<td>Final boiling point (K)</td>
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<tr>
<td>Flash point (K)</td>
</tr>
<tr>
<td>Freezing point (K)</td>
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<tr>
<td>Density at 15°C (kg/l)</td>
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<tr>
<td>Viscosity at −20°C (mm²/s)</td>
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<tr>
<td>Net heat of combustion (MJ/kg)</td>
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<tr>
<td>Conductivity (pS/m)</td>
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<tr>
<td>Lubricity test (BOCLE) wear scar (mm)</td>
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<tr>
<td>Aromatics (% vol)</td>
</tr>
<tr>
<td>Total sulfur (% mass)</td>
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<tr>
<td>Hydrogen content (% mass)</td>
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</tbody>
</table>
in Oklahoma. The specification properties of this fuel are presented in Table 1. A blend of 32% iso-octane, 25% n-decane, and 43% n-dodecane [33] was employed as the surrogate for the GTL fuel chemical kinetics study. The initial mixture composition for GTL/air mixture is defined as

\[
\phi (0.32 \text{C}_8\text{H}_{18} + 0.25 \text{C}_{10}\text{H}_{22} + 0.43 \text{C}_{12}\text{H}_{26}) + 15.83 (\text{O}_2 + 3.76\text{N}_2)
\]

This surrogate mixture has an empirical formula of \( \text{C}_{10.22}\text{H}_{22.44} \), H/C ratio of 2.196, an estimated cetane number of 61, and a molecular weight of 145.37 g/mol.

### Results and Discussion

**Chemical Mechanisms Comparison.** While development of the chemical 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 [33,34,36,43]. These mechanisms are summarized in Table 2. As shown in this table, in terms of computational cost, Dooley et al. mechanism [34] is the most expensive mechanism due to the large number of species, and Yu et al. mechanism [36] is the least expensive mechanism. All three surrogates of iso-octane, n-decane, and n-dodecane are included in Naik et al. [33], Dooley et al. [34], and Ranzi et al. [43] mechanisms except Yu et al. mechanism [36] which only has two surrogates of 2,5-dimethylhexane and n-dodecane. So, 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 [36], its own suggested composition of 41.9% 2,5-dimethylhexane and 58.1% n-dodecane has been used.

Figure 1 shows a comparison of ignition delay times between available chemical mechanisms [33,34,36,43] of GTL fuel with the heated shock tube experimental data of Wang and Oehlschlager [23] at an equivalence ratio of 1 and a pressure of 20 atm for temperatures varying from 700 K to 1300 K. As it can be seen, Dooley et al. mechanism [34] overestimates the values of ignition delay time especially for low and intermediate temperatures. For time-dependent calculations such as ignition delay time, Naik et al. mechanism [33] is valid only for high-temperature conditions \( T > 1000 \text{K} \) as shown in Fig. 1, whereas for the time-independent calculations such as laminar burning speed [46–48], it is valid for a wide range of temperatures, which will be discussed later. Figure 1 also shows that both Ranzi et al. [43] and Yu et al. [36] mechanisms have a good agreement with the experimental results but the agreement of Ranzi et al. [43] mechanism with intermediate temperature is slightly better.

For laminar burning speed prediction, the steady one-dimensional premixed flame code from CANTERA [45] has been used. Dooley et al. [34] mechanism due to large computational time has not been considered in this comparison. Figures 2 and 3 show the comparison of laminar burning speed for different chemical mechanisms [33,36,43] over a wide range of equivalence ratios at 1 atm and at temperatures of 400 K and 473 K, respectively. As it can be seen, all the mechanisms are close to each other but Ranzi et al. [43] mechanism has slightly better agreement with the experimental data. Since the agreement of Ranzi et al. [43] mechanism with experimental data for ignition delay time and laminar burning speed is slightly better, and also, it includes all three surrogates of iso-octane, n-decane, and n-dodecane, therefore, it is selected for further analysis in this study.

#### Ignition Delay Time

Figure 4 shows the ignition delay time predicted using Ranzi et al. [43] mechanism for a wide range of temperatures of 650–1650 K at six different pressures of 1, 10, 20, 30, 50, and 100 atm. As it can be seen that increasing the pressure at a given temperature decreases the ignition delay time or in other words, increases the auto-ignition propensity [49]. At low temperatures \( T < 800 \text{K} \), the effect of pressure on ignition delay

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<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. [33]</td>
<td>753</td>
<td>7007</td>
<td>Iso-octane, n-decane, and n-dodecane</td>
</tr>
<tr>
<td>Dooley et al. [34]</td>
<td>3164</td>
<td>21,671</td>
<td>Iso-octane, n-decane, and n-dodecane</td>
</tr>
<tr>
<td>Ranzi et al. [43]</td>
<td>484</td>
<td>19,341</td>
<td>Iso-octane, n-decane, and n-dodecane</td>
</tr>
<tr>
<td>Yu et al. [36]</td>
<td>373</td>
<td>2037</td>
<td>2,5-dimethylhexane and n-dodecane</td>
</tr>
</tbody>
</table>

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**Table 2 Comparison of different chemical mechanisms for GTL fuel**

**Fig. 1 Comparison of ignition delay time between available GTL chemical mechanisms [33,34,36,43] and experimental data [23] at equivalence ratio of 1 and pressure of 20 atm for a wide range of temperatures**

**Fig. 2 Comparison of laminar burning speed between GTL chemical mechanisms [33,36,43] and experimental data [22,28,30] for different equivalence ratios at pressure of 1 atm and temperature of 400 K**
Time is negligible, whereas it has a significant effect at intermediate and high temperatures ($T > 800$ K). Temperature has a very interesting effect on ignition delay time as shown in Fig. 4. At high-temperature conditions ($T > 1000$ K) for a given pressure, the ignition delay time decreases with an increase in temperature. In this case, the temperature has a negative dependency to ignition delay time. This trend is changed to positive dependency for intermediate temperatures and again switched to negative dependency for low temperatures. The change in dependency occurs at higher temperatures as pressure increases. Figure 4 also shows that pressure has a minor effect on ignition delay time for low temperatures, and the effect of pressure increases by increasing the temperature. It can be concluded from this figure that for low-temperature conditions, the ignition delay time is a strong function of temperature.

The ignition delay time for GTL/air mixture for a wide range of temperatures and three different equivalence ratios is predicted using the DKM model. The results are shown for three different pressures of 10, 50, and 100 atm in Figs. 5–7, respectively. As shown, at a given temperature, increasing the equivalence ratio decreases the ignition delay time and increases the auto-ignition propensity. It is observed that there is also a shift in trends at high-temperature conditions. For a pressure of 10 atm, this shift occurs around 1380 K as shown in Fig. 5.

Fig. 3 Comparison of laminar burning speed between GTL chemical mechanisms [33,36,43] and experimental data [22,28,29,38] for different equivalence ratios at pressure of 1 atm and temperature of 473 K

Fig. 4 Theoretical ignition delay time for a wide range of temperatures at three different equivalence ratios and a pressure of 10 atm using Ranzi et al. [43] mechanism for GTL/air mixture

Fig. 5 Theoretical ignition delay time for a wide range of temperatures at three different equivalence ratios and a pressure of 50 atm using Ranzi et al. [43] mechanism for GTL/air mixture

Fig. 6 Theoretical ignition delay time for a wide range of temperatures at three different equivalence ratios and a pressure of 100 atm using Ranzi et al. [43] mechanism for GTL/air mixture

Fig. 7 Theoretical ignition delay time for a wide range of temperatures at three different equivalence ratios and a pressure of 100 atm using Ranzi et al. [43] mechanism for GTL/air mixture
moves toward high-temperature direction as the pressure goes up.

Effect of pressure on laminar burning speed and flame thickness is shown in Fig. 9. As it is shown, pressure has a negative relationship with both laminar burning speed and flame thickness. As the pressure increases, both laminar burning speed and flame thickness decrease. For example, the laminar burning speed and flame thickness decrease from 112.8 to 53.8 cm/s and 0.28 to 0.028 mm, respectively, as the pressure increases from 1 to 25 atm at an equivalence ratio of 1.1. However, the rate of reduction of laminar burning speed and flame thickness becomes slower as the pressure increases.

### Conclusions

In this work, the ignition and laminar burning speed characteristics of GTL fuel were predicted by developing a DKM from the existing mechanisms for the GTL fuel. A mixture of 32% iso-octane, 25% n-decane, and 43% n-dodecane was used as the surrogate fuel to mimic the chemical composition of the GTL jet fuel (S-8) from Syntroleum Corporation. Different chemical kinetic mechanisms reported in the literature were tested over a wide range of operating conditions. Among them, the Ranzi et al. chemical mechanism was found to have a better agreement with the experimental data. Therefore, in this study, the laminar burning speed and ignition delay time were investigated using CANTERA and DKM, respectively, using Ranzi’s mechanism. The key highlights of the predictions are as follows:

- Starting from low temperature, the ignition delay time for GTL first decreases as the initial temperature increases for low temperature ($T < 800$ K), then increases at intermediate temperature ($800-1000$ K), and finally decreases again for high-temperature range ($T > 1000$ K). Higher pressure increases the ignition propensity.
- A shift in trends for different equivalence ratio is observed for GTL auto-ignition. If initial temperature is lower than the shifting temperature, higher equivalence ratio decreases the ignition delay time. After temperature passed the shifting point, the ignition delay time increases as the equivalence ratio increases.
- The laminar burning speed reaches its maximum value at equivalence ratio equal to 1.1. The highest laminar burning speed of GTL increases from 66.8 cm/s to 267.2 cm/s as the temperature increases from 400 to 800 K.
- The minimum of flame thickness happens at equivalence ratio of 1.2, where the flame is very vulnerable to hydrodynamic instability because of the reduction in flame thickness.
- Initial pressure has a negative effect on the laminar burning speed. The laminar burning speed drops from 112.8 cm/s to 53.8 cm/s as the pressure increases from 1 to 25 atm.

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