

The Development of an Ignition Delay Correlation for PRF Fuel Blends from PRF0 (n-Heptane) to PRF100 (iso-Octane)

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ABSTRACT

A correlation was developed to predict the ignition delay of PRF blends at a wide range of engine-relevant operating conditions. Constant volume simulations were performed using Cantera coupled with a reduced reaction mechanism at a range of initial temperatures from 570-1860K, initial pressures from 10-100atm, oxygen mole percent from 12.6% to 21%, equivalence ratios from 0.30-1.5, and PRF blends from PRF0 to PRF100. In total, 6,480 independent ignition delay simulations were performed.

The correlation utilizes the traditional Arrhenius formulation; $\tau = A\phi^\alpha p^\beta x_{O_2}^\gamma \exp(\lambda)$ with equivalence ratio (ϕ), pressure (p), and oxygen mole percentage (x_{O_2}) dependencies. The exponents α , β , and γ were fitted to a third order polynomial with respect to temperature with an exponential roll-off to a constant value at low temperatures to capture the behavior expressed by the reaction mechanism. The location and rate of the roll-off functions were modified by linear functions of PRF. The activation energy term, λ is expressed as a combination of a third and second order polynomial with respect to temperature with an exponential roll-off function whose location and rate varied with a second order function with respect to PRF to capture the differences between PRF blends in the NTC region. The resulting correlation contains 41 constants with an average standard deviation of $\pm 24\%$ compared to the reaction mechanism values in the range of interest to engine applications.

Auto-ignition predictions were calculated using the Livengood-Wu auto-ignition integral and compared to experimental HCCI heavy-duty engine data. The predictions were calculated using two different methods, the first utilized the ignition delay correlation developed in this work, and the second method utilized linear interpolation between relevant points in a large matrix populated by 58,443 ignition delay values. Both predictions showed good agreement ($\pm 1.5^\circ\text{CA}$) with the start of combustion from the HCCI engine data under the operating conditions tested.

CITATION: DelVescovo, D., Kokjohn, S., and Reitz, R., "The Development of an Ignition Delay Correlation for PRF Fuel Blends from PRF0 (n-Heptane) to PRF100 (iso-Octane)," *SAE Int. J. Engines* 9(1):2016, doi:10.4271/2016-01-0551.

INTRODUCTION

In an effort to avoid the pollutant emissions associated with conventional diesel and spark ignited (SI) engines in an environment of increasingly stringent emissions regulations [1], researchers have turned towards low temperature combustion (LTC) strategies, such as homogenous charge compression ignition (HCCI) [2,3,4], premixed charge compression ignition (PCCI) [5], and reactivity controlled compression ignition (RCCI) [6,7,8], among others in an effort to reduce peak cylinder temperatures, and avoid oxides of nitrogen (NO_x) and particulate matter (PM) formation without costly exhaust aftertreatment [1]. These combustion strategies are highly sensitive to fuel chemical kinetics, and therefore require well defined and robust chemical mechanisms to perform the simulation work that is a necessary component of advanced combustion development.

Premixed fueling strategies such as HCCI, PCCI, and RCCI require a detailed description of fuel kinetics through an incredibly wide operating space in terms of temperature, pressure, and mixture composition in order to accurately predict combustion parameters, such as start of combustion (SOC), crank angle of 50% of mass fraction burned (CA50), and combustion duration (CA10-90), necessary for direct control of a combustion system utilizing such a strategy. Dual fuel strategies such as RCCI require not only well defined chemistry for one fuel, but for two separate fuels and all potential mixtures of the two. To assist in the design and development of such advanced strategies, it is beneficial to turn to simplified computational models of the combustion process for predicting combustion behavior and trends in order to provide better control methods and algorithms necessary for advanced combustion implementation and optimization [9,10,11].

Primary reference fuel (PRF) blends are often used as chemical surrogates for both gasoline and diesel fuels [6,12], and the ignition delays of PRF fuels have been extensively studied in shock tubes, rapid compression machines (RCM), and constant volume (CV) chambers [1,13,14]. Algebraic expressions for ignition delay have been developed for various fuels including iso-octane (PRF100) [9,15], and n-heptane (PRF0) [16,17] as a means of correlating experimental data, and to examine the effect of various parameters such as pressure, temperature, equivalence ratios, etc., on the fuel chemistry [9,15,16].

Ignition delay correlations can avoid the use of large, computationally intensive, detailed chemical mechanisms to quickly predict ignition delay, which can be coupled with an auto-ignition predicting algorithm to model engine relevant parameters such as knock in SI applications [18], and start of combustion [19,20] and thermal stratification [10] in HCCI applications. These applications require the ignition delay correlations to accurately and robustly match the actual fuel chemistry over a wide range of operating conditions [9,18]. As discussed by Goldsborough [9,18], ignition delay correlations can be a computationally efficient means of incorporating model based control methods into an engine controlsystem, however existing correlations need to demonstrate good agreement particularly in the low temperature and negative temperature coefficient (NTC) regimes to produce adequate results over the large operating space of conventional and advanced engine platforms [18], particularly in applications such as HCCI combustion where combustion stability and noise are highly sensitive to intake charge conditions and fuel chemistry [18].

IGNITION DELAY SIMULATIONS

Ignition delay simulations were performed using a constant volume reactor in Cantera coupled with a reduced gasoline surrogate mechanism [21] obtained from the Lawrence Livermore National Laboratory (LLNL) website. The mechanism has 323 species. This mechanism was chosen in order to be able to run a large number of ignition delay cases in a reasonable amount of computational time as the average run time was ~10s, compared to ~80s for the LLNL 679 species mechanism [22] and ~1500s for the LLNL detailed mechanism [23]. The CV reactor input conditions (temperature, pressure, species mole fractions) were varied parametrically to provide a wide operating space to develop the correlation. Equivalence ratio (ϕ) is defined here as the fresh air equivalence ratio, and the oxygen mole percentage (x_{O_2}) is the percentage of oxygen in the gas that does not include the fuel to eliminate the influence of ϕ on x_{O_2} . Because of this, x_{O_2} can be related to the exhaust gas recirculation (EGR) fraction by the relationship in Eq. (1) (assuming that the inlet air is 21% by mole O_2). In total, 6,480 ignition delay simulations were performed covering the ranges listed in Table 1. These initial conditions were selected as they are representative of the range of conditions seen in conventional combustion and advanced combustion modes.

Table 1. Cantera CV chamber simulation initial conditions for correlation

Parameter	Range	Number of Cases
Temperature	570-1860K	18
Pressure	10-100atm	4
x_{O_2}	12.6-21%	3
ϕ	0.3-1.5	6
PRF	0-100	5

$$x_{O_2} = 21\% * (1 - EGR)$$

(1)

Ignition delay was defined as the time at which the maximum temperature rise rate occurred with the additional condition that the final temperature was greater than or equal to 400K above the initial temperature. This condition insured that the ignition delay would be representative of the high temperature heat release (HTHR) and would ignore any low temperature heat release (LTHR) behavior present at the particular condition. Figure 1 shows the definition of ignition delay used in the following work. This definition of ignition delay introduces some measure of uncertainty when comparing to experimental HCCI cases which exhibit significant LTHR behavior as discussed in [27, 11]. Both of these authors propose the use of an alternative integral method which takes into account both the LTHR or “cool-flame” ignition delay, and the HTHR ignition delay, however only the HTHR ignition delay is considered here, the implications of which will be discussed in following sections.

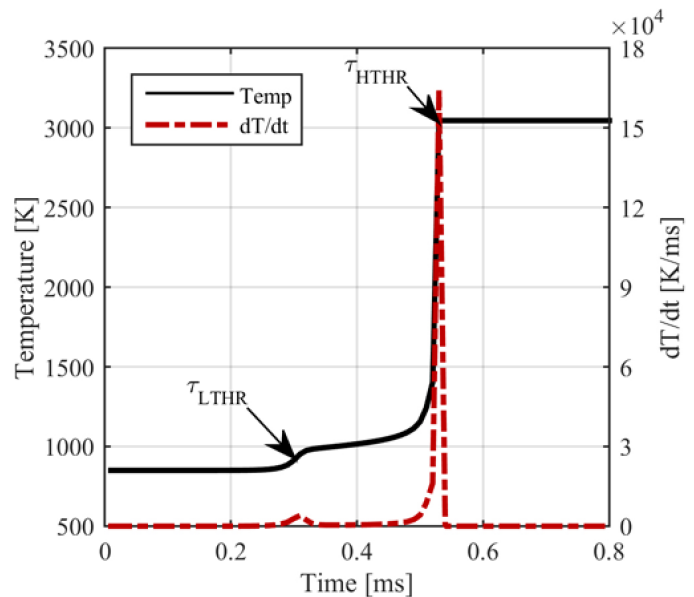


Figure 1. Constant volume temperature and derivative of temperature from Cantera depicting the definition of ignition delay at $T_{initial} = 850K$, $p = 50atm$, $x_{O_2} = 21\%$, $\phi = 1.0$, for PRF0, including locations of LTHR ignition delay and HTHR ignition delay.

FORMULATION OF CORRELATION

The functional form of the ignition delay chosen in this work was the commonly used Arrhenius-based power law formulation. This formulation has been applied by numerous researchers [9,15,16,17]

for modeling the ignition delay of hydrocarbon fuels including nheptane and isooctane. The general form of this equation is:

$$\tau = A\phi^\alpha p^\beta x_{O_2}^\gamma \exp(\lambda), \quad (2)$$

where ϕ is the fresh air equivalence ratio, p is the pressure, x_{O_2} is the oxygen mole percentage of the diluent gas, and the traditional activation energy term E_a/RT in the exponential is replaced by the term λ to remain consistent with the work of Goldsborough [9] in his ignition delay correlation for iso-Octane (PRF100). Goldsborough's method for determining the values of the coefficients in Eq. (2) is employed throughout this work, and is expanded to all PRF mixtures. Solving Eq. (2) for each parameter value separately under the listed conditions yields Eqs. (3, 4, 5) for α , β , and λ respectively.

$$\alpha_{param} = \frac{\ln(\tau_2/\tau_1)}{\ln(\phi_2/\phi_1)}; \quad \phi_1 = 1.0 \quad (3)$$

where: $T_2 = T_1$, $p_2 = p_1$, $x_{O_2} = x_{O_2}$, $PRF_2 = PRF_1$

$$\beta_{param} = \frac{\ln(\tau_2/\tau_1)}{\ln(p_2/p_1)}; \quad p_1 = 50atm \quad (4)$$

where: $T_2 = T_1$, $\phi_2 = \phi_1$, $x_{O_2} = x_{O_2}$, $PRF_2 = PRF_1$

$$\gamma_{param} = \frac{\ln(\tau_2/\tau_1)}{\ln(x_{O_2}/x_{O_2})}; \quad x_{O_2} = 21\% \quad (5)$$

where: $T_2 = T_1$, $\phi_2 = \phi_1$, $p_2 = p_1$, $PRF_2 = PRF_1$

Typically the α , β , γ , and activation energy are considered to be constants. As illustrated by Goldsborough in [9], this approach did not adequately capture the behavior of PRF100 in the NTC region. Figure 2 shows the parameter values for the α , β , and γ terms using Eqs. (3, 4, 5) respectively for PRF100 and PRF0 as a function of inverse temperature ($T^* = 1000/T$). The curve fits assume the same functional form as Goldsborough used in his iso-octane correlation [9]. The functions are third order polynomials with respect to T^* , with an exponential roll-off function in the NTC region to a constant value at low temperature (high T^*). These plots highlight the differences in the calculated parameter values for the two fuels, most notably in the NTC region (where T^* is between ~ 1.2 to 1.5). It is evident that the most significant difference between the curve fits for PRF0 and PRF100 are in the location of the roll-off function, and the rate of the roll-off, that is, in the extremes of the plot in terms of T^* , the parameter values for PRF0 and PRF100 tend to converge.

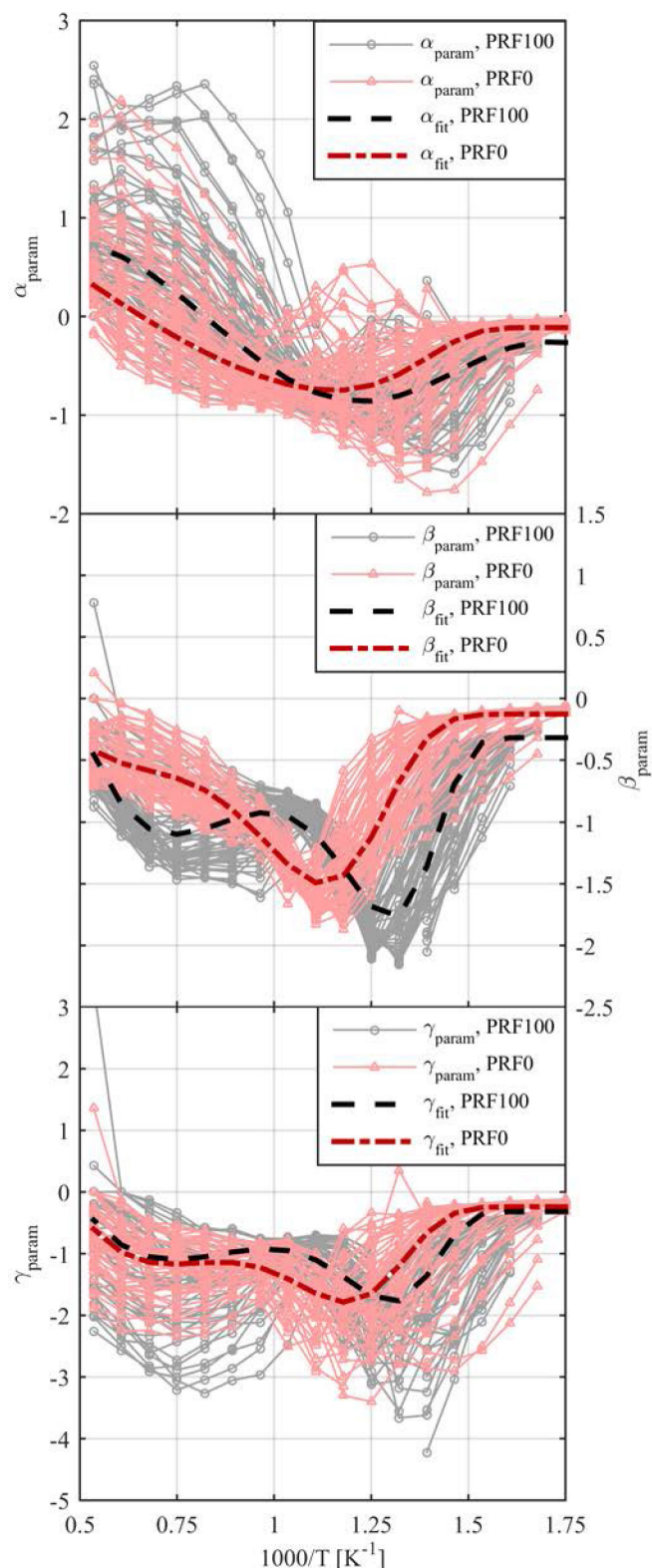


Figure 2. Parameter values as a function of inverse temperature for PRF100 and PRF0, comparing the sensitivity to ϕ , p , and x_{O_2} , of the two fuels as a function of temperature respectively. Thin solid lines represent the parameter values relative to the baseline condition for each combination of p , x_{O_2} , and ϕ simulated, the dashed lines represent the functional curve fit of the data.

The correlation developed in this work uses the same functional form for the α , β , and λ parameters as Goldsborough with modifications to the exponential roll-off temperature and exponent that are linear functions of PRF. This modification adjusts the parameter values in the NTC region to account for the differences present in the mechanism in ϕ , p , and x_{O_2} sensitives for the PRF mixtures seen in Figure 2. The functional forms of the parameter values can be seen in Eqs. (6, 7, 8) where α , β , and λ correspond to the exponents in Eq (2).

$$\alpha = \alpha' + \left(\sum_{i=0}^3 a_i T^{*i} \right) \times \exp \left\{ - \left[\frac{T^*}{(T_{\alpha}^* + dT_{\alpha}^* \times PRF)} \right]^{(n_{\alpha} + dn_{\alpha} \times PRF)} \right\} \quad (6)$$

$$\beta = \beta' + \left(\sum_{i=0}^3 b_i T^{*i} \right) \times \exp \left\{ - \left[\frac{T^*}{(T_{\beta}^* + dT_{\beta}^* \times PRF)} \right]^{(n_{\beta} + dn_{\beta} \times PRF)} \right\} \quad (7)$$

$$\gamma = \gamma' + \left(\sum_{i=0}^3 c_i T^{*i} \right) \times \exp \left\{ - \left[\frac{T^*}{(T_{\gamma}^* + dT_{\gamma}^* \times PRF)} \right]^{(n_{\gamma} + dn_{\gamma} \times PRF)} \right\} \quad (8)$$

The three parameters have identical functional forms, and the coefficients of the functions were determined using Matlab's built-in Curve Fitting Toolbox. A Levenberg-Marquardt algorithm and bisquare regression were selected in the Curve Fitting Toolbox, and care was taken in determining the initial values for the curve fitting to insure an appropriate solution. The resulting functions were then compared qualitatively to the parameter values to obtain adequate agreement between the curve fit and the data.

The result of the parameter curve fitting can be seen in Figure 3. The function forms chosen in Eqs. (6, 7, 8) provide show similar behavior to the curve fits for the individual fuels in Figure 2, especially in the NTC region which is the region of primary interest. At high temperatures (low T^*), the PRF mixtures collapse onto a single line that is effectively the average parameter value for all the PRF mixtures. This formulation will lead to some amount of error in the high temperature regime as a result. The equivalence ratio and pressure sensitivity in the high temperature regime in this correlation will more closely resemble those of the intermediate PRF mixtures (PRF25-PRF75) as a result of the averaging in this region. Another significant deviation of this formulation from the mechanism results is the temperature of sign change for the equivalence ratio sensitivity. As discussed in [9], this cross-over point is the temperature at which the chain-branching $H+O_2=O+OH$ reaction begins to dominate

ignition. For iso-octane, this temperature is near 1150K ($T^* = 0.87$) [13]. The sign change associated with the chain branching reaction occurs much later ($T^* \sim 0.75$, $T \sim 1333K$) using this formulation.

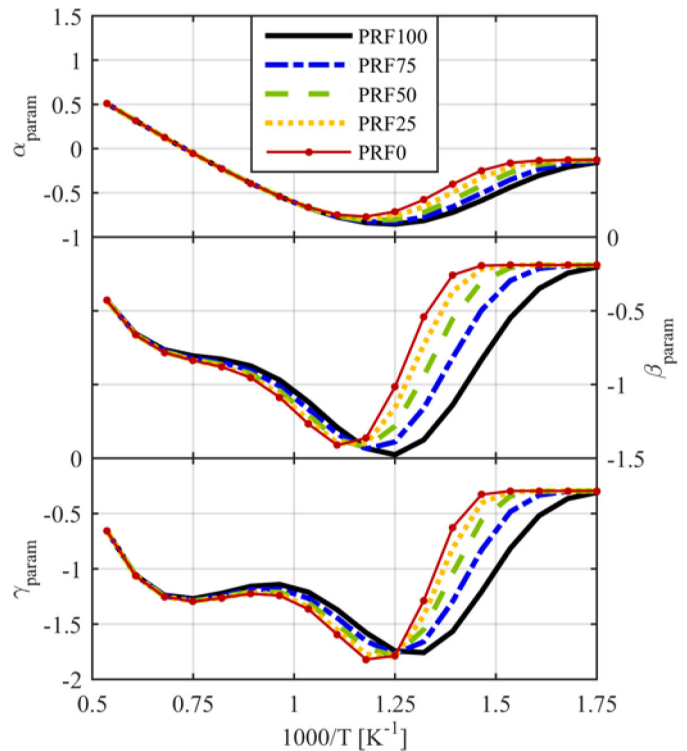


Figure 3. α_{param} (solid lines), β_{param} (dashed lines), and γ_{param} (dotted lines) vs. inverse temperature for five PRF mixtures showing the influence of PRF on each parameter value.

With the α , β , and γ terms fit, the activation energy term can be solved for using Eq. 9. The value of the scaling coefficient, A , is set to 1.0 in this work.

$$\lambda_{param} = \ln \left(\frac{\tau}{A \phi^{\alpha} p^{\beta} x_{O_2}^{\gamma}} \right) \quad (9)$$

The value of λ_{param} was determined for each value of T , ϕ , p , and x_{O_2} , and PRF tested in the study. In order to determine the functional form of λ_{param} , the parameter value was plotted vs. T^* for PRF100 and PRF0 in Figure 4 to examine the effect of PRF and temperature on the activation energy term. For the purposes of making Figure 4, the values of α , β , and γ were only functions of temperature, and used the curve fits shown in Figure 2. The λ functions were curve fit using the functional form used by Goldsborough [9], ignoring the pressure dependent term. As expected, the n-heptane exhibits a lower activation energy relative to iso-octane in the NTC region and at low temperatures. Interestingly, however, around 1000K the activation energy term for PRF100 is lower than that of PRF0. The behavior of the two fuels in the intermediate and high temperature region is the inverse of the trend seen in this region in the β term (Figure 2).

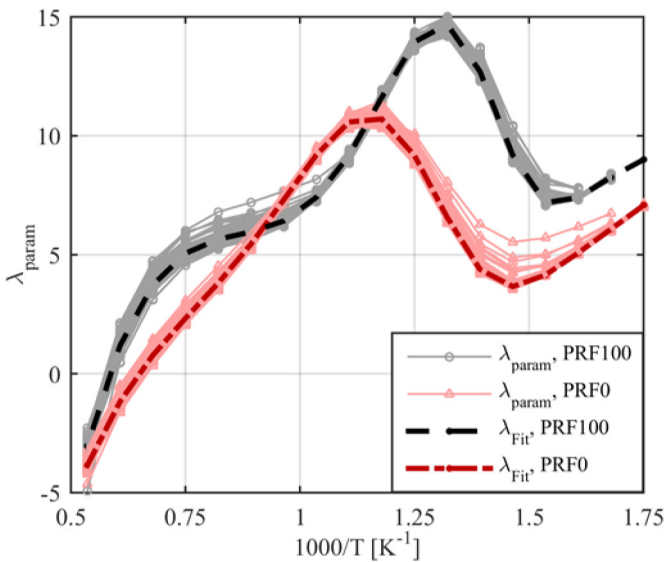


Figure 4. λ_{param} vs. inverse temperature for PRF100 and PRF0, comparing the activation energy term of the two fuels as a function of temperature. Thin solid lines represent each value of λ_{param} calculated parametrically from Eq. (9). Dashed lines represent the curve fit of the data.

The pressure dependency in Goldsbrough's correlation on the activation energy term is ignored in this work, and activation energy is considered to only be a function of temperature and PRF. This simplification is made because, as Goldsbrough discusses, the chemical mechanism used in his work shows a much weaker pressure dependency than the experimental data [9], and significant pressure dependency was not evident in the conditions tested here. Therefore, since this work uses only the chemical mechanism for ignition delay prediction, the pressure dependent term is eliminated.

A similar modification to the one made previously for the parameter values α , β , and γ is made to Goldsbrough's formulation of the λ term to account for the differences in the activation energy term for PRF blends in the NTC region. For the activation energy term, the exponential roll-off function utilizes a second order function of PRF instead of the linear function of PRF used for the α , β , and γ terms. The second order functionality provides a better fit to the parameter values for the range of PRF. Eq. 10 shows the functional form of the λ term.

$$\lambda = \sum_{i=0}^2 d_i T^{*i} - \left[\sum_{i=0}^2 d_i T^{*i} - \sum_{i=0}^3 e_i T^{*i} \right] \times \exp \left\{ - \left[\frac{T^*}{(T_{\lambda}^* + \sum_{i=1}^2 dT_{\lambda i}^* \times PRF^i)} \right]^{(n_{\lambda} + \sum_{i=1}^2 dn_{\lambda i} \times PRF^i)} \right\} \quad (10)$$

Figure 5 depicts the final curve fits for the various PRF mixtures as a function of inverse temperature. The curve fit captures the decreasing activation energy in the NTC region with decreasing PRF very well.

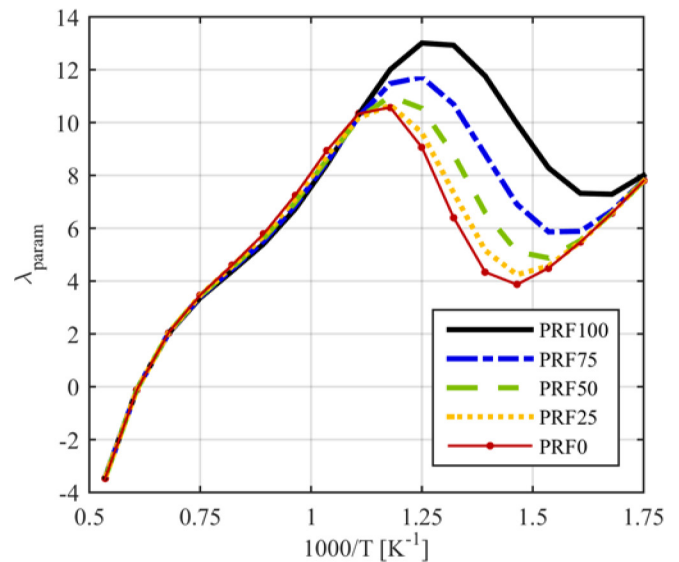


Figure 5. λ_{param} vs. inverse temperature for five PRF mixtures, showing the influence of PRF on the λ_{param} .

The λ term can be related to the activation energy through the relationship seen in Eq. 11, where A' is a scaling factor used to normalize the activation energy term for comparison purposes. In this work, $A' = 3.57 \times 10^{-7}$ and $A = 1$. This value for A' comes from Goldsbrough's work in [9], and is used to provide direct comparisons between the activation energy predicted in his work for PRF100 and this work.

$$E_a = RT[\lambda + \ln(A/A')] \quad (11)$$

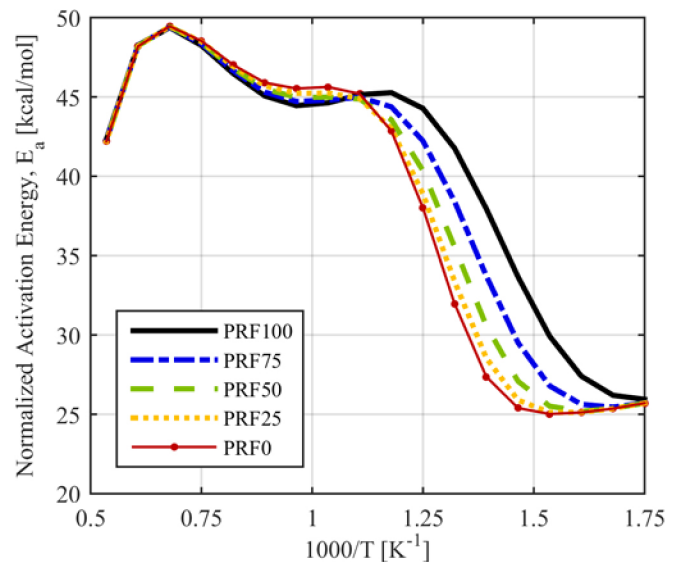


Figure 6. Normalized activation energy vs. inverse temperature for five PRF mixtures, showing the effect on activation energy of PRF.

The activation energies predicted for iso-octane in this work compare very favorably with the values seen in Goldsbrough's work between T^* of 0.9 to 1.75 [9]. But in the very high temperature region ($T^* > 0.75$), the activation energy predicted is much higher than the activation energy predicted by Goldsbrough. Davidson et al. [10]

reported similar values of activation energies for n-heptane and isooctane at temperatures above 1100K, which agrees well with the behavior seen in Figure 6.

Table 2. Parameter values for the developed PRF correlation

Parameter	Value	Parameter (cont)	Value
A	1.0	γ'	-0.2956
α'	-0.1301	γ_0	16.78
a_0	2.228	γ_1	-65.79
a_1	-3.123	γ_2	80.55
a_2	0.1977	γ_3	-32.57
a_3	0.1887	T_y^*	1.276
T_{α}^*	1.334	dT_y^*	0.0001591
dT_{α}^*	0.001179	n_y	12.53
n_a	9.495	dn_y	-0.05869
dn_a	-0.01916	d_0	9.314
β'	-0.1896	d_1	-19.54
b_0	10.53	d_2	10.67
b_1	-42.87	e_0	132.2
b_2	55.54	e_1	-454.4
b_3	-24.35	e_2	528.4
T_{β}^*	1.199	e_3	-215.2
dT_{β}^*	0.0003184	T_{λ}^*	1.196
n_{β}	10.27	$dT_{\lambda 1}^*$	9.683e-6
dn_{β}	-0.04541	$dT_{\lambda 2}^*$	4.592e-6
		n_{λ}	8.538
		$dn_{\lambda 1}$	-0.02678
		$dn_{\lambda 2}$	-2.063e-5

The values of the constants used in Eqs. (6, 7, 8 and 10) are shown in Table 2. Figure 7 shows a plot of ignition delay vs. inverse temperature comparing the correlation with the ignition delay values from Cantera for various PRF values at the condition listed.

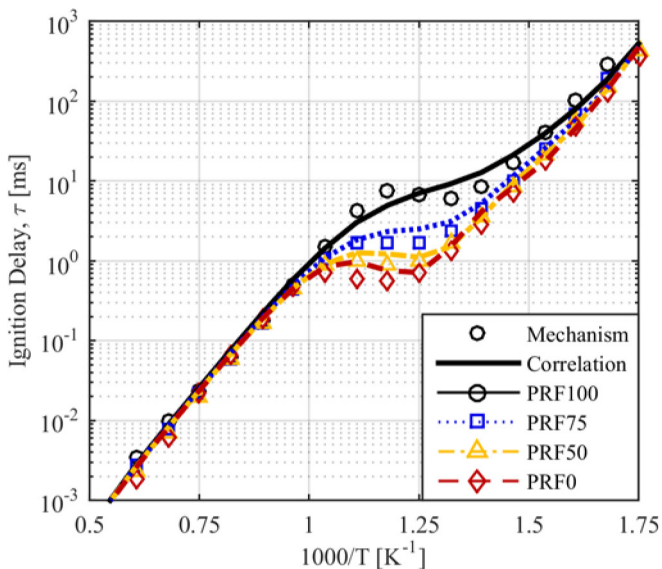


Figure 7. Ignition delay vs. inverse temperature from Cantera (symbols) and the developed correlation (lines) at $p = 50\text{atm}$, $\phi = 1.0$, and $x_{O_2} = 21\%$ for various PRF mixtures.

The correlation shows good agreement with the ignition delays from Cantera, however the discrepancy between the correlated and the actual values is greater for the pure PRF blends (PRF0 and PRF100) than for intermediate PRF blends (PRF25, PRF50, PRF75). More

plots comparing the predicted and actual ignition delays showing the pressure, equivalence ratio, and oxygen percentage sensitivity for PRF0, PRF50, PRF75 and PRF100 can be found in the Appendix.

Quantification of Error

Figure 8 shows a plot of the percent error between the ignition delays predicted using the correlation developed in the previous section and the ignition delays from Cantera. Positive error is defined as an ignition delay that is less than the actual value, and negative error is defined as an ignition delay that is greater than the actual value to indicate the direction of the deviations in the correlation. The data shows good agreement, with a standard deviation (σ) of $\pm 28\%$ for the 6,480 cases tested which compares favorably to the σ of $\pm 34\%$ reported by Goldsborough for his 37-coefficient iso-octane correlation [9]. The major source of the relatively high standard deviation shown here is the assumed lack of functionality of the parameters in the Arrhenius expression to pressure, ϕ , and x_{O_2} . More complete relationships could be developed that include such functionality at the cost of greater complexity.

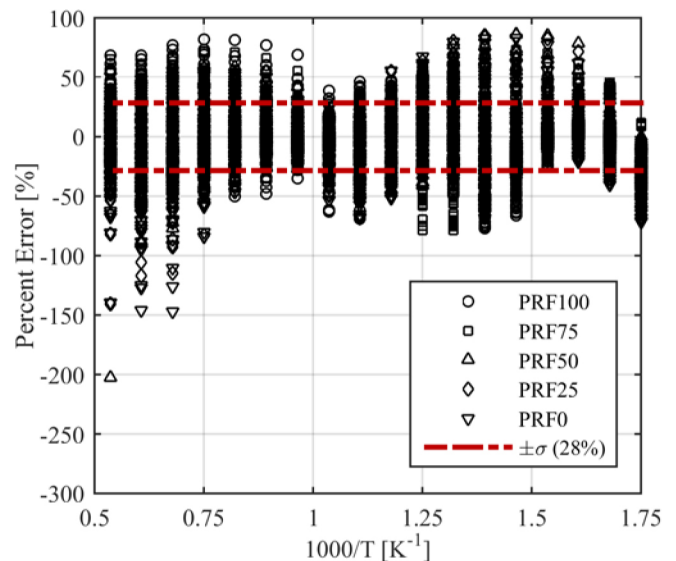


Figure 8. Scatter plot of percent error of the predicted ignition delay from the correlation compared to the ignition delay values from the mechanism at all the tested conditions vs. inverse temperature. The red line corresponds to the average standard deviation (28% in this case) of all the cases. (Y-axis cuts off two data points $< -300\%$ error at the very high T end of the plot).

At very high temperatures there are points that deviate significantly, predicting much larger ignition delays than expected. This potentially occurs because the functional form chosen for the activation energy parameter forces convergence of all the PRF blends to a single line at high temperatures as can be seen in Figure 5. Alternatively this may be an artifact of the error metric which amplifies small relative errors when the magnitude itself is small. Nevertheless, in the high temperature region, it may be beneficial to use an alternate ignition delay correlation which better captures high temperature behavior.

An alternate method to represent the data in Figure 8 is to plot a scatter plot of the calculated ignition delays from the correlation vs. the ignition delays from the CV simulation. This can be seen in Figure 9.