

Ignition Delay Correlation for Predicting Autoignition of a Toluene Reference Fuel Blend in Spark Ignition Engines

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ABSTRACT

An ignition delay correlation was developed for a toluene reference fuel (TRF) blend that is representative of automotive gasoline fuels exhibiting two-stage ignition. Ignition delay times for the autoignition of a TRF 91 blend with an antiknock index of 91 were predicted through extensive chemical kinetic modeling in CHEMKIN for a constant volume reactor. The development of the correlation involved determining nonlinear least squares curve fits for these ignition delay predictions corresponding to different inlet pressures and temperatures, a number of fuel-air equivalence ratios, and a range of exhaust gas recirculation (EGR) rates. In addition to NO_x control, EGR is increasingly being utilized for managing combustion phasing in spark ignition (SI) engines to mitigate knock. Therefore, along with other operating parameters, the effects of EGR on autoignition have been incorporated in the correlation to address the need for predicting ignition delay in SI engines operating with EGR. Unlike the ignition delay expressions available in literature for primary reference fuel blends, the correlation developed in the present study can predict ignition delay for a TRF blend, a more realistic gasoline surrogate.

1. INTRODUCTION

Two of the means to achieve the objective of improved fuel economy in spark ignition (SI) engines are (a) improving the fuel conversion (thermal) efficiency by increasing the compression ratio, and (b) increasing the specific output (brake power per unit displacement) through turbocharging and downsizing the engine. The ability to raise in-cylinder peak pressures in either mechanism is, however, limited by knock. Accurate prediction of autoignition phasing is thus critical in designing engines with improved efficiency. Clearly, such a prediction also is pertinent to the homogeneous charge compression ignition (HCCI) technology, which relies on controlled autoignition through compression of the homogeneously mixed oxidizer-fuel mixture. Detailed chemical kinetic mechanisms can be employed to predict autoignition. However, their sheer complexity presents a serious challenge in terms of directly incorporating them in engine simulation or computational fluid dynamics (CFD) tools. Therefore, there is a need for a computationally feasible autoignition model that accurately captures the complexity of fuel oxidation in SI engines under varying operating conditions and is easy to use. This need has prompted the development of empirical autoignition models. A pressure-temperature correlation of the form

$$\tau = Ap^{-n} \exp\left(\frac{B}{T}\right) \quad (1)$$

for predicting ignition delay in SI engines, which is based on empirical data and employs a global Arrhenius reaction rate was first introduced by Livengood and Wu [1], In Eq. (1), τ is the ignition delay; p and T are the in-cylinder pressure and temperature, respectively; and A , B , and n are constants. The derivation of Eq. (1) is based on the assumption that the functional relationship between the concentration ratio $[M]/[M]_c$ and time t is given by

$$\frac{[M]}{[M]_c} = \int_{t=0}^{t=t_c} \frac{1}{\tau} dt = 1.0, \quad (2)$$

where $[M]$ is the concentration of products of the overall combustion reaction, and $[M]_c$ the concentration at the time of autoignition $t = t_c$. This concept was further developed by Rifkin *et al.* [2], Burwell and Olson [3], and Vermeer *et al.* [4]. Douaud and Eyzat [5] introduced a fuel dependent term in Eq. (1) by expressing the constant A as

$$A = C_1 \left(\frac{AKI}{100} \right)^{C_2}, \quad (3)$$

where C_1 and C_2 are fit coefficients, and antiknock index $AKI = 0.5 \times (RON + MON)$ is the average of the research octane number (RON) and motor octane number (MON). Efforts have been made to improve the ignition delay correlation [of Eq. (1)] by modifying the fit coefficients [6,7], and incorporating fuel concentration [8] and fuel-air equivalence ratio [9,10] in the ignition delay correlation. While modified versions of the Douaud and Eyzat [5] model are commonly used in engine simulation tools, these models all assume the combustion initiation point can be modeled with a single global reaction rate. These empirical models do not capture the *cool flame* phenomenon exhibited by saturated hydrocarbons (or paraffins) of the form C_nH_{2n+2} with $n > 2$ [11] which is a consequence of the negative temperature coefficient (NTC) of reaction rate. Competition between chain branching and terminating steps results in decreasing reaction rates as temperature increases, hence the term “negative temperature coefficient”. This NTC behavior manifests itself in paraffin oxidation as two-stage ignition. The termination of the first stage ignition is a result of the inhibited branching, also known as degenerate branching. This mechanism is commonly referred to as the low temperature kinetic scheme because of the modest temperature rise associated with it. The chain terminating steps become dominant and prevent the mixture from completely reacting to reach its adiabatic flame temperature. An induction time follows until branching again becomes

dominant, leading to the second stage or hot ignition where the majority of heat is released. Figure 1 illustrates temperature profiles for single and two-stage ignition typically observed in a constant volume reactor (CVR) for a TRF blend. It is evident from Fig. 1 that for two-stage ignition, the oxidation reaction proceeds in two distinct phases and this phenomenon cannot be captured with a single global reaction rate. As saturated hydrocarbons are a significant constituent of automotive gasoline fuels, it is imperative that the autoignition models capture the details of two-stage ignition to provide accurate ignition delay predictions.

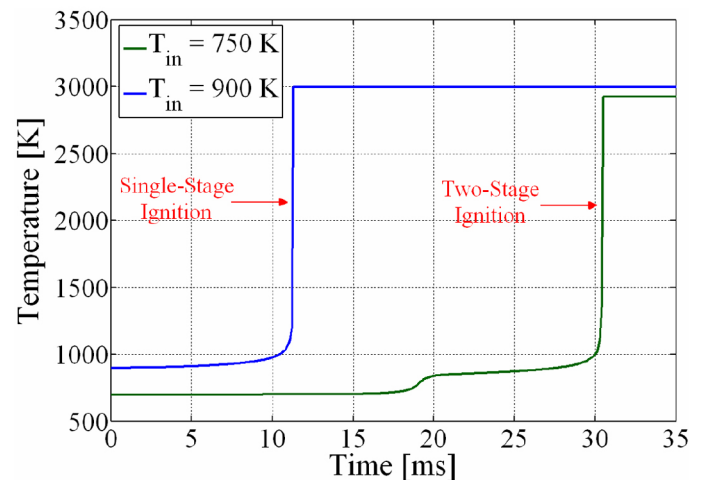


Figure 1. Single and two-stage ignition [Reactor: CVR; Fuel: TRF 91].

Yates and Viljoen [12] and Yates *et al.* [13] have developed an empirical ignition delay correlation that characterizes the effects of the cool flame phenomenon by calculating the overall ignition delay in two stages. This improved correlation addresses the fundamental drawback of autoignition models confined to a single global reaction rate. However, it is important to note that this correlation was initially calibrated for *primary reference fuel* (PRF) blends. Unlike PRF blends which are binary mixtures of the paraffins *n*-heptane (C_7H_{16}) and *iso*-octane (C_8H_{18}), commercial gasoline is a complex blend of several different species which can be broadly classified into paraffins, olefins, aromatics, and naphthalenes (cycloparaffins) based on their molecular structure. The presence of aromatics and olefins significantly alters the chemical kinetics of the oxidation process, as unlike paraffins, they do not exhibit NTC behavior. Leppard [14] has shown that the NTC behavior becomes more pronounced with decreasing pressures, increasing temperatures, and decreased reaction times. These changes in operating parameters are consistent with those encountered in moving from the RON test to the MON test conditions. As paraffins exhibit NTC behavior, they are more resistant to autoignition under MON rating conditions compared to olefins and

aromatics. Therefore unlike a PRF blend for which the RON and MON ratings are identical, a fuel blend that includes aromatics and olefins will have a lower MON rating than its RON rating. As gasoline blends are composed of several different species including aromatics and olefins they are octane sensitive with different RON and MON ratings. Since aromatic compounds are a major component (~30%) of gasoline [15,16], unlike PRF blends, fuel blends including aromatic compounds can capture the fuel octane sensitivity of gasoline fuels. Availability of well established detailed chemical kinetic mechanisms for toluene, an aromatic, makes it a suitable candidate for modeling the effect of aromatics in gasoline. Therefore, a TRF blend has been selected in the present study for the kinetic modeling.

The objective of this work is to develop an improved empirical ignition delay correlation for a TRF 91 blend. Ignition delay predictions for operating conditions covering a wide range of inlet pressures p_{in} , inlet temperatures T_{in} , fuel-air equivalence ratios ϕ , and EGR rates obtained from detailed chemical kinetic simulations performed in CHEMKIN [17] are used to develop the correlation.

Section 2 briefly discusses the kinetic modeling performed in CHEMKIN and Section 3 describes in detail the development of the improved ignition delay correlation. Results and discussion are presented in Section 4, followed by concluding remarks in Section 5.

2. KINETIC MODELING

Hydrocarbon oxidation is a complex chemical process involving a large number of different species and reactions. Most of the radicals and intermediates involved in combustion reactions are typically very short lived and are formed in small quantities. Consequently, their detection and measurement is difficult. This makes chemical kinetic models an indispensable tool for understanding the combustion mechanisms. Since knock is a fundamental problem in SI engines, one of the main objectives of kinetic modeling efforts has been to accurately capture the autoignition event. As the knocking tendency of the binary mixtures of *n*-heptane and *iso*-octane in a Cooperative Fuel Research (CFR) engine is used to assign octane ratings to fuels, the oxidation chemistry of these two PRFs has been studied extensively, leading to the development of several reduced [18,19,20], skeletal [21], and global [22] kinetic mechanisms. The combustion chemistry group at the Lawrence Livermore National Laboratory (LLNL) has compiled a detailed kinetic mechanism for PRF oxidation by combining *n*-heptane [23] and *iso*-octane [24] oxidation mechanisms. This mechanism is comprised of 1034 species and 4238 reactions, and is referred to as PRF (LLNL). Toluene ($C_6H_5CH_3$) is one of the more prominent aromatic components of gasoline fuels [16]. This has prompted numerous experimental studies using shock tubes, rapid compression machines (RCM), flow

reactors, and jet-stirred reactors to determine the characteristics of toluene oxidation. Lindstedt and Maurice [25] proposed one of the first detailed kinetic mechanisms for toluene combustion. This mechanism has since been further developed for a wide range of pressure and temperature conditions [26,27,28,29]. Andrae *et al.* [30] have combined a toluene oxidation submechanism with the PRF (LLNL) mechanism to develop a detailed chemical kinetic scheme for the autoignition of TRFs. Andrae [31] has developed a detailed kinetic mechanism for gasoline surrogate fuels by combining his earlier mechanism [30] with submechanisms for diisobutylene and ethanol. This mechanism is comprised of 1121 species and 4961 reactions and will be hereafter referred to as the Surrogate (Andrae). All predictions for the TRF 91 oxidation presented in this study were obtained using the Surrogate (Andrae) mechanism.

Simulating reaction systems with detailed chemical kinetic mechanisms is computationally intensive as it requires the solution of a large number of stiff differential equations. CHEMKIN, a computer software originally designed at Sandia National Laboratories, facilitates the formulation, solution, and interpretation of a wide range of combustion problems involving gas-phase and surface kinetics, and gas transport. It features a large variety of flame simulators, flow components, and reactor models, including the *closed homogeneous constant volume reactor* or CVR. Knock is typically observed in SI engines when the piston is near top dead center (TDC), at which point the volume of the combustion chamber does not change very rapidly and the surface area of the combustion chamber is at its minimum. Due to the relatively little change in volume of the combustion chamber, reduced surface area for heat loss, and the small time scales involved, autoignition may be approximated as a constant volume adiabatic process. This approximation allows the effects of various engine operation parameters to be studied qualitatively in a CVR. In addition, a CVR is analogous to the compressed volumes in rapid compression machines and shock tubes, allowing comparisons between CVR predictions and RCM/shock tube experiments. Since the CVR facilitates the study of a complex problem like knock in a somewhat simplified manner, it has been used for performing all simulations in this work.

3. MODELING APPROACH ADOPTED FOR DEVELOPING IMPROVED IGNITION DELAY CORRELATION

The ignition delay correlation proposed here builds upon the model originally developed by Yates and Viljoen [12] and later refined by Yates *et al.* [13] at the Sasol Advanced Fuel Laboratory, or the Sasol model. As indicated in Section 1, the Sasol model captures the cool flame effect by modeling the overall ignition delay in two stages. For a two step process,

the conservation-of-delay principle [Eq. (2)] of Livengood and Wu [1] can be rewritten as

$$\int_{t_0}^{t_1} \frac{dt}{\tau_{h,in}} + \int_{t_1}^{t_{AI}} \frac{dt}{\tau_{h,CF}} = 1, \quad (4)$$

where t_0 represents the start of the combustion process, t_1 is the time from the start of the reaction to the first stage ignition which coincides with the appearance of the cool flames, and t_{AI} is the overall ignition delay (see Fig. 2). In Eq. (4) $\tau_{h,in}$ and $\tau_{h,CF}$ represent the characteristic exothermic reaction delays evaluated at the initial and post cool flame conditions, respectively. The characteristic exothermic reaction delay can be described as the time from the start of the reaction to the ultimate heat release for a single step process governed by a global reaction rate. Therefore, $\tau_{h,in}$ and $\tau_{h,CF}$ are essentially the time delays corresponding to two different global reactions. Assuming constant pressure and temperature during each stage and $t_0 = 0$, Eq. (4) simplifies to

$$\frac{t_1}{\tau_{h,in}} + \frac{t_{AI} - t_1}{\tau_{h,CF}} = 1. \quad (5)$$

Equation (5) can be rearranged to obtain the overall ignition delay

$$t_{AI} = t_1 + \tau_{h,CF} \left(1 - \frac{t_1}{\tau_{h,in}} \right), \quad (6)$$

where

$$t_1 = \phi^{\beta_1} A_1 p_{in}^{n_1} e^{\frac{B_1}{T_{in}}}, \quad (7)$$

$$\tau_{h,in} = \phi^{\beta_h} A_h p_{in}^{n_h} e^{\frac{B_h}{T_{in}}}, \quad (8)$$

and

$$\tau_{h,CF} = \phi^{\beta_h} A_h p_{CF}^{n_h} e^{\frac{B_h}{T_{in} + X \Delta T_{CF}}}. \quad (9)$$

In Eqs. (7,8,9) p_{in} is the inlet pressure, T_{in} is the inlet temperature, p_{CF} is the post cool flame pressure, ϕ is the fuel-air equivalence ratio, and ΔT_{CF} is the temperature rise associated with the first stage ignition and is defined as

$$\Delta T_{CF} = \omega \left(T_{in} - T_{EQ} p_{in}^{\kappa} \phi^{\mu} \left(\frac{100}{99 + \phi} \right)^{\sigma} \right). \quad (10)$$

Yates and Viljoen [12] have observed that as T_{in} increases the cool flame temperature rise ΔT_{CF} decreases. As ΔT_{CF} in Eq. (10) is a linear function of T_{in} , it can yield negative values for ΔT_{CF} at high T_{in} . Since negative values for ΔT_{CF} are physically not feasible, Yates and Viljoen [12] introduced the termination function

$$\Delta T_{CF} = 0.5 \left(\Delta T_{CF} + \sqrt{(\Delta T_{CF})^2 + C_0} \right) \quad (11)$$

to prevent ΔT_{CF} from becoming negative. In Eqs. (7,8,9,10,11) β_1 , A_1 , n_1 , B_1 , β_h , A_h , n_h , B_h , X , ω , T_{EQ} , κ , μ , σ , and C_0 are coefficients determined from nonlinear least squares curve fits.

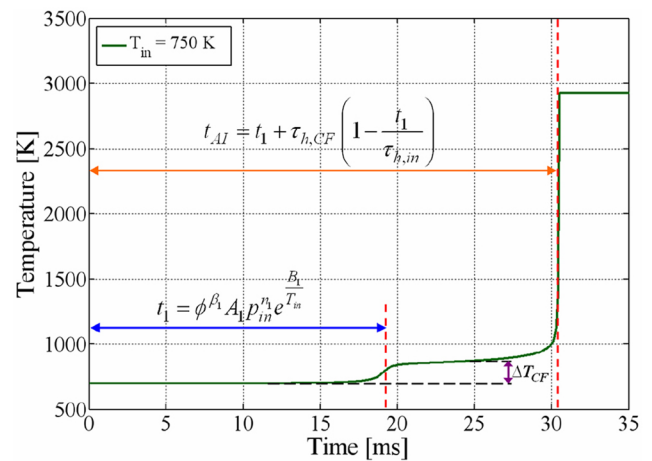


Figure 2. Description of the different terms associated with the Sasol model.

The Sasol model was first developed for PRF blends with octane number (ON) ranging from 0 to 100 [12] and later augmented to predict ignition delay for blends of PRFs with methanol [12] and ethanol [13]. In current work, the basic structure of the Sasol model has been retained with the focus on developing an ignition delay correlation for a TRF 91 blend (53.8% i -C₈H₁₈, 13.7% n -C₇H₁₆, and 32.5% C₆H₅CH₃ by liquid volume) that also accounts for the effect of EGR on autoignition. In addition to controlling NO_x, EGR is increasingly used to control combustion phasing and mitigate knock in contemporary SI engines. It is imperative that an effective knock prediction tool capture the effect of EGR on autoignition. The ignition delay correlation proposed here has been developed to address this need and captures the effects of EGR on autoignition in addition to p_{in} , T_{in} , and ϕ . To develop the correlation for TRF 91, ignition delay predictions were obtained from CVR simulations for 1710 distinct cases, including 3 different inlet pressures $p_{in} = 12, 25$, and 40 bar; 19 different inlet temperatures over the range $650 \leq T_{in} \leq 1200$ K; 5 different fuel-air equivalence ratios, covering the

range $0.8 \leq \phi \leq 1.2$ in 0.1 increments; and 6 different exhaust gas recirculation (EGR) rates spanning the range $0 \leq EGR \leq 25\%$ in 5% increments.

The present work models EGR as a mixture of CO_2 , H_2O , and N_2 (the products of complete combustion of the fuel) and introduces it into the CVR at the same p_{in} and T_{in} as the fuel-air mixture. In order to incorporate EGR in the ignition delay correlation, the effect of EGR on t_1 , ΔT_{CF} , and t_{AI} was examined. It was observed with increasing EGR, t_1 and t_{AI} increase for all p_{in} , as depicted in Fig. 3 (both in linear and logarithmic scales for ignition delay) by colored open and solid symbols, respectively. At a given T_{in} , the cool flame temperature rise ΔT_{CF} decreases with increasing EGR for all p_{in} , as illustrated in Fig. 4. Also, due to the lower heat release during the first stage ignition with increasing EGR, the induction time between the first and second stage ignition, $t_{Induction} = t_{AI} - t_1$, increases (open black symbols in Fig. 3). The EGR term was introduced in the correlation in a manner that resembles the equivalence ratio term. Thus, the first stage ignition delay t_1 was proposed here to be of the form

$$t_1 = \left(1 + \frac{EGR\%}{100}\right)^{r_1} \phi^{\beta_1} A_1 p_{in}^{n_1} e^{\frac{B_1}{T_{in}}}. \quad (12)$$

Similarly, the two characteristic exothermic reaction delays $\tau_{h,in}$ and $\tau_{h,CF}$ were defined as

$$\tau_{h,in} = \left(1 + \frac{EGR\%}{100}\right)^{r_h} \phi^{\beta_h} A_h p_{in}^{n_h} e^{\frac{B_h}{T_{in}}}, \quad (13)$$

and

$$\tau_{h,CF} = \left(1 + \frac{EGR\%}{100}\right)^{r_h} \phi^{\beta_h} A_h p_{CF}^{n_h} e^{\frac{B_h}{T_{in} + X \Delta T_{CF}}}. \quad (14)$$

Finally, the cool flame temperature rise ΔT_{CF} in Eq. (14) is expressed as

$$\Delta T_{CF} = \omega \left(T_{in} - T_{EQ} p_{in}^{\kappa} \phi^{\mu} \left(\frac{100}{99 + \phi} \right)^{\sigma} \left(1 + \frac{EGR\%}{100} \right)^{r_{CF}} \right). \quad (15)$$

The form of the proposed EGR term as $\left(1 + \frac{EGR\%}{100}\right)$ ensured that it contributed to increasing t_1 and t_{AI} and decreasing ΔT_{CF} for $EGR > 0\%$. Therefore, the new correlation is

comprised of Eq. (6) along with Eqs. (11,12,13,14,15) instead of Eqs. (7,8,9,10,11).

In order to obtain the overall ignition delay from Eq. (6), the fit coefficients associated with Eqs. (11,12,13,14,15) need to be ascertained. These coefficients are obtained from nonlinear least squares curve fits to ignition delay predictions obtained from CHEMKIN for individual p_{in} as a function of T_{in} . The curve fitting process involves three steps:

STEP 1: FIRST STAGE IGNITION DELAY

As discussed in Section 1, the cool flame phenomenon is associated with the competition between chain branching and terminating steps. Therefore at high T_{in} , where the chain branching steps dominate, the cool flame phenomenon was not observed. To determine the coefficients for Eq. (12), the initial delay time t_1 was first ascertained from CHEMKIN simulations, for the cases where first stage ignition is observed, as the time from the start of the reaction to the point of maximum temperature rise gradient. Next Eq. (12) is expressed as a linear relation

$$\ln t_1 = r_1 \left(1 + \frac{EGR\%}{100} \right) + \beta_1 \ln \phi + \ln A_1 + n_1 \ln p_{in} + B_1 / T_{in} \quad (16)$$

and fit to the t_1 values obtained from CHEMKIN for a specific ϕ and EGR combination, as illustrated in Fig. 5. While Eq. (16) is linear in nature, t_1 varies non-linearly at high temperatures ($T_{in} > 750$ K) in Fig. 5. As T_{in} increases, high temperature kinetics start dominating and the reaction system starts shifting from the two-stage to the single-stage ignition regime. The first stage ignition becomes difficult to detect and the cool flame temperature rise approaches zero, resulting in the non-linear variation of t_1 with increasing T_{in} . Thus, to avoid inclusion of cases in which the occurrence of the first stage ignition is questionable, the curve fits are obtained only for the region where t_1 varies linearly with inlet temperature, $T_{in} \leq 750$ K in this case, to provide the values for the coefficients β_1 , A_1 , n_1 , B_1 , and r_1 .

STEP 2: FIRST STAGE IGNITION TEMPERATURE RISE

In this work ΔT_{CF} was defined as the difference between the temperature at the midpoint of the induction period after the first stage ignition and T_{in} . As the first stage ignition was not observed at high T_{in} , ΔT_{CF} values can be determined from CHEMKIN simulations only for the cases where the first stage ignition is discernable. Equation (15) was fit to the ΔT_{CF} values obtained from CHEMKIN as illustrated in Fig. 6 to determine the coefficients ω , T_{EQ} , κ , μ , σ , and r_{CF} .