

A New Functional Global Auto-ignition Model for Hydrocarbon Fuels - Part 1 of 2: An Investigation of Fuel Auto-Ignition Behaviour and Existing Global Models

2010-01-2161

Published
10/25/2010

Gareth Floweday

Sasol Advanced Fuels Laboratory, Mechanical Engineering Department, University of Cape Town

Copyright © 2010 SAE International

ABSTRACT

Homogeneous Charge Compression Ignition (HCCI) engine technology has been an area of rapidly increasing research interest for the past 15 years and appears poised for commercialisation through the efforts of international research institutions and manufacturers alike. In spite of significant worldwide research efforts on numerous aspects of this technology, the need still exists for accurate and computationally efficient fuel auto-ignition models capable of predicting the heat release dynamics of two-stage auto-ignition, especially for full boiling range fuels, sensitive to the effects of pressure, temperature, fuel equivalence ratio and inert dilution.

This study was the first of a two part investigation in which analysis of published alkane fuel oxidation kinetic schematics, detailed fuel auto-ignition behavioural studies and critical evaluation of existing global model formulations (Part 1) provided insight for the formulation of a new functional global auto-ignition model (Part 2).

Part 1 was conducted by focussing on three inter-relating aspects:

1. Published literature relating to the modelling of hydrocarbon chemical kinetics was reviewed and analysed in detail including schematics of alkane combustion chemical kinetics.
2. The basic observable characteristics of fuel auto-ignition reactions were systematically studied using detailed chemical kinetic simulations as being closely representative of the real-life physical and chemical phenomena.

3. Existing global auto-ignition models were critically evaluated in comparison with the functional requirements identified in the auto-ignition behavioural study.

Part 1 therefore provides foundational insights and functional requirements for the modelling of fuel auto-ignition for application in the study of HCCI engines.

INTRODUCTION

HCCI engine technology promises significant improvements in efficiency and emissions compared with current gasoline and diesel engine technologies [1,2,3]. HCCI engines do, however, pose significant challenges relating to the control of the phasing and rate of fuel combustion processes. For this reason engine thermodynamic and combustion processes have been targeted areas of research in this field [1,2]. Currently available engine thermodynamic models and combustion auto-ignition models vary widely in complexity and functionality [4,5,6,7,8,9,10]. Combination of these models for HCCI engine research generally results in significant computational expense and therefore poses a challenge in terms of balancing simulation run times and required accuracy. A significant international research effort has been directed towards addressing this challenge, with the publishing of various reduced [11,12,13,14], skeletal [15,16,17,18,19,20,21], global [22,23,24,25] and empirical [8,9,26,27,28,29,30,31] fuel auto-ignition models.

This Part 1 study sought to examine the chemistry and behavioural attributes of hydrocarbon fuel auto-ignition in order to assess existing global fuel auto-ignition models and formulate the functional requirements for an improved global auto-ignition model.

**Documents**

Document Sharing Hub

Table 1. Categories of chemical kinetic models (taken directly from [25])

Category	Description	Species	Reactions
Detailed	the latest “comprehensive” reaction set	100’s	1000’s
Lumped	uses a lumped description for larger species	100’s	1000’s
Reduced	a subset of the detailed model	10’s	10’s- 100’s
Skeletal	employs class chemistry and lumping concepts	10’s	10’s
Global	utilizes global reactions to minimize reaction set	<10	<10

A BRIEF REVIEW OF THE STUDY OF FUEL AUTO-IGNITION

THE EXPERIMENTAL BASIS FOR FUEL AUTO-IGNITION MODELLING

A wide range of experimental auto-ignition data is available in the literature, including testing of numerous fuels, from single component fuels, through surrogate blends to full boiling range fuels. A valuable summary of the experimental data (available prior to 1995) from a wide variety of auto-ignition test devices has been provided in [32]. This has been recently complemented with the summary of subsequent experimental auto-ignition studies found in [33]. Experimental auto-ignition studies have been conducted using rapid compression machines (RCMs) [34,35,36,37], shock tubes [38;39], constant volume vessels, flow tubes, jet-stirred reactors, mechanically stirred flow reactors, flat flame burners, motored engines and variations of these devices. One of the primary reasons for the wide variety in auto-ignition testing devices is the fact that available devices have limitations in the range of temperature and pressure at which the fuel can be tested.

FUEL OXIDATION CHEMISTRY

While discussion of the intricacies of detailed fuel auto-ignition is beyond the scope of this work, schematics of hydrocarbon reaction kinetics are widely available in the literature [1;18;25;30,31,32;34;35;40;41]. Although these schematics are by nature simplifications of the detailed processes involved, they provide some insight into the dominant chemical pathways and resulting kinetic behaviour. For the purposes of this study, the reactions schematic for alkane fuels presented by Zhao et al. [1] was used as a reference for auto-ignition model structures, since it shows good general agreement with other schematics in the literature and was written in the context of HCCI combustion studies. The first 13 reactions of the schematic are presented in [Appendix A](#) for convenient reference. Zhao et al. [1] included seven additional reactions in the high temperature

region. These involved various chain branching reactions involving hydrogen, hydroxyl, oxygen, hydroperoxy and water species. These reactions were stated [1] as being extremely reactive and therefore occur at very high reaction rates. These reaction details were therefore considered outside of the scope of this study.

FUEL AUTO-IGNITION MODELING APPROACHES

Modern numerical combustion studies have been divided into a number of methodologies generally related to the level of detail required and associated computational expense afforded. Zheng et al. [25] defined the commonly used classifications as shown in [Table 1](#).

A comprehensive review of lumped, reduced, skeletal and global models, their development and experimental validation, has been provided by Griffiths [32]. An additional category of fuel auto-ignition model is the empirical model. This sixth category is not included in [Table 1](#) because empirical models are not true rate based kinetic models.

Detailed chemical kinetics mechanisms

Detailed chemical kinetic mechanisms aim to provide the complete set of active chemical reaction permutations for a given overall reaction. As chemical kinetic models have incorporated progressively larger molecules, these mechanisms have “exploded” in size and detailed models incorporating many thousands of reactions and over a thousand species are now available[41;42]. An extensive review of hydrocarbon detailed kinetic modelling has been provided by [43] and more recently by [33]. Due to the extensive validation used in the development of detailed kinetic mechanisms [42;44,45,46] and the challenges of obtaining agreement from experimental auto-ignition data sources, researchers often use the predictions of detailed kinetic models to validate the performance of their reduced models [7], skeletal models [21], global models [4;23;24] and empirical ignition delay models [9;30;31]. While validating a

model with another model may be regarded as poor scientific practice in other fields, the practice in this field is generally accepted and even encouraged [32].

Reduced chemical kinetics mechanisms

Many of the possible reactions making up a detailed kinetics mechanism have limited influence on the function of the mechanism or its numerical predictions [32;47] and can be removed, especially where reduced functionality or range is acceptable for the application. Various techniques have been developed to reduce detailed mechanisms to the subset of dominant reactions, including sensitivity, reaction lumping, reaction flow, extended lifetime analysis, quasi-steady-state analysis (QSSA), “brute force”, Morris-one-at-a-time and Monte-Carlo methods [11;32]. Recent examples of such reduction studies are provided by [11,12,13,14].

Skeletal auto-ignition models

Skeletal mechanisms afford much better opportunity for parameter solving and uncertainty studies than reduced mechanisms due to their significantly reduced complexity and chemistry class lumping approach [12].

Researchers at the Shell Thornton Research Centre developed a generalised skeletal model consisting of 11 reactions for all hydrocarbon fuels [15]. This model was later developed [22] to comprise of 8 reactions and 7 species and this model became known as the “Shell model”. This original Shell model may be better classified as a global auto-ignition model, but is included in this section because it formed the basis for most of the later developed skeletal models discussed below. Automated parameter optimisation of this model was attempted in [22], while [48] developed a mathematical method for reducing its computational expense.

The Shell model [22] was extended by Cox and Cole [16] to 15 generalised reactions involving 10 species. This extension incorporated a more detailed description of the chain propagation of alkylperoxy radical isomerisation and oxidation in that the 2nd oxygen addition and internal hydrogen abstraction were not lumped together with the first sequence.

Hu and Keck [17] further developed the work of Cox and Cole [16] and formulated a reduced mechanism consisting of 18 reactions and 13 active species. A further reduced model consisting of the first 10 reactions of their scheme was discussed and appeared to agree fairly well with the experimental data, even in the absence of additional tuning. Consideration of the model in relation to various alkane fuels indicated that only the first H abstraction equilibrium reaction constant was affected by fuel structure.

Li et al. [18] further developed the Hu and Keck reduced auto-ignition model, adding an additional 11 reactions and 5

species to obtain a better agreement with total heat released. The additional reactions catered for oxidation of aldehydes, olefins, carbonyls as well as the formation of carbon dioxide and its oxidation to carbon trioxide (CO₃) to reduce overall heat release. This model was developed further in [19] by adding a further 11 reactions and 7 species to form a model consisting of 29 reactions and 20 active species.

This 29 reaction model was further extended by Zheng et al. [20] by incorporating the high temperature reactions from the Griffiths unified model [14]. The model was aimed at HCCI applications and consisted of 69 reactions and 45 active species.

A versatile skeletal mechanism was recently developed by Machrafi et al. [21] for the gasoline and diesel surrogate blend components: iso-octane, n-heptane and toluene. The mechanism was developed by merging 3 reduced mechanisms of the respective pure components and incorporating some additional simplifications (such as removing details of the extremely high temperature kinetics) to result in the surrogate mechanism comprising 62 reactions and 49 species.

Global auto-ignition models

Müller et al. [23] developed a 4-step (5 reactions in total) skeletal model to describe n-heptane auto-ignition. The model used 2 reactions for the high temperature (HT) chemistry and two reactions for the low temperature (LT) chemistry with the first LT reaction being reversible. This model produced reasonable agreement to experiments for such a simple model and obtained the characteristic low temperature “S” shaped ignition delay vs. temperature behaviour. The model could not, however, obtain true Negative Temperature Coefficient (NTC) behaviour (increasing ignition delay for increasing temperature) due to the lack of chain branching species and thermal dependency of the model, and has attracted criticism regarding this weakness [24;32].

Schreiber et al. [24] developed a 5-step (6 reactions in total) mechanism for Primary Reference Fuel (PRF) blends in an attempt to resolve the above mentioned shortcomings of [23]. The model used the reversible reaction and the chain branching species to produce NTC behaviour, resulting in improved accuracy of ignition delay prediction. However, the temperature-time traces revealed a lack of accuracy in the cool-flame heat release timing, shape and magnitude predictions. The model also defied Hess' law (the heat release of the HT path was higher than that of the LT path) and the heat releasing final reaction was not dependant on the reactant fuel species, thereby allowing the reaction to continue after the fuel was depleted.

Zheng et al. [25] developed an improved global mechanism for PRF mixtures. The model used a 7-step scheme (nine

reactions in total) and included the reversible formation and dissociation of carbon monoxide and carbon dioxide in the high temperature chemistry. Experimental validation across different PRF blends was not given and claimed validity for model sensitivity to the effects of pressure and air-fuel ratio was weakly presented. Prediction of overall ignition delay (ID) was reasonably good for the results shown. However, in spite of cool flame heat release prediction being a primary aim of the study, the authors admitted that "... the model does not predict the discrete temperature and heat release jump that was observed experimentally."

Bourdon et al. [4] developed the 5-step scheme proposed by Schreiber [24]. Some valuable modifications were made to the original model, such as compliance to Hess' Law and inclusion of fuel concentration dependence in the fifth reaction. The model optimisation was done using a genetic algorithm, but the fitness function was based purely on overall ignition delay, without inclusion of cool-flame heat release dynamics. The model showed reasonable agreement with the detailed kinetics on overall ignition delay although understandably (due to the fitness function definition) it showed poor cool-flame dynamics agreement. The model was then incorporated into a 3D Computational Fluid Dynamics (CFD) code to simulate HCCI combustion of n-heptane, achieving reasonable run times (5 hours) on a standard desktop computer.

Empirical auto-ignition models

In 1955 Livengood & Wu [26] developed a simple empirical approach to the calculation of ignition delay where an Arrhenius delay expression was integrated over the pressure-temperature time history experienced by the fuel-air mixture. This later became known as the Knock-Integral approach to ignition delay prediction [8;9]. Despite the crude basis of the model, it was shown that the model worked well for single stage auto-ignition prediction. Livengood and Wu acknowledged that 2-stage ignition and deflagration reactions would not be well described by this model and a double ignition integral approach was suggested for the former case [26]. The single Arrhenius Knock Integral approach was further developed for octane prediction by Douaud and Eyzat [27] and also used for HCCI auto-ignition modelling by Swan et al. [9] and Shahbakhti et al. [8].

Yates et al. [28] developed a 3-part Arrhenius auto-ignition model capable of good agreement to the overall ignition delay times of NTC fuels. This work was extended [29;30] using the vehicle knock limited spark advance data, Research Octane Number (RON) and Motor Octane Number (MON) test data and detailed chemical kinetics simulations of a variety of fuels. Yates and Viljoen [31] subsequently developed an Arrhenius empirical model for predicting the cool-flame timing, cool flame temperature rise and overall auto-ignition delays of PRF and methanol blends. The model

was calibrated to fit a wide range of pressures, temperatures and fuel equivalence ratios, but did not include inert exhaust product dilutants. The model's auto-ignition delay prediction was applied by using the "knock integral method" in various HCCI studies [5;49;50].

FUEL AUTO-IGNITION BEHAVIOURAL STUDY

BASIS FOR THE BEHAVIOURAL STUDY

In view of the recent success of the Yates and Viljoen auto-ignition model [31] in predicting two-stage auto-ignition dynamics and the number of more complex models available for reference, the development of a global model with accurate two-stage auto-ignition predictive functionality was pursued by the author of this study.

Further understanding of fuel auto-ignition behavioural characteristics was pursued through the use of detailed chemical kinetic simulations. Over 2200 detailed chemical kinetic simulations were run for iso-octane, n-heptane, 1-hexene, toluene, methanol and a quaternary gasoline surrogate suggested by [46] consisting of iso-octane, toluene, hexene and n-heptane in the molar ratio 44/30/18/8%. These simulations were run as perfectly stirred, constant volume reactor simulations using the detailed mechanism from [42]. The simulations covered a wide range of experimental conditions of temperature, pressure, fuel equivalence ratio and inert exhaust product dilution. General background to single and two-stage fuel auto-ignition characteristics, including "cool flame" and main heat release dynamics can be found in literature [30,31,32,33;40;51]. Insights gained regarding various aspects of the behavioural characteristics of fuel auto-ignition are described in the sections below.

TEMPERATURE EFFECTS ON TWO- STAGE AUTO-IGNITION

Figure 1 illustrates a number of significant temperature effects on the auto-ignition characteristics of the 2-stage fuel, n-heptane. In this figure label (and subsequent labels) P refers to the constant pressure value of the simulation, Phi refers to the fuel-air equivalence ratio and R refers to the mass percentage of reaction product or exhaust residual dilution included in the starting air-fuel mixture. For ease of deciphering the inverted temperature scale, the light grey series allows the initial temperature (T_i) to be read across onto the secondary y-axis. For the purpose of this study, the following definitions were used:

- The cool flame ignition delay (CFID) was defined as the elapsed time corresponding to the first peak in the derivative of temperature w.r.t. time for a fuel exhibiting a two-stage heat release.

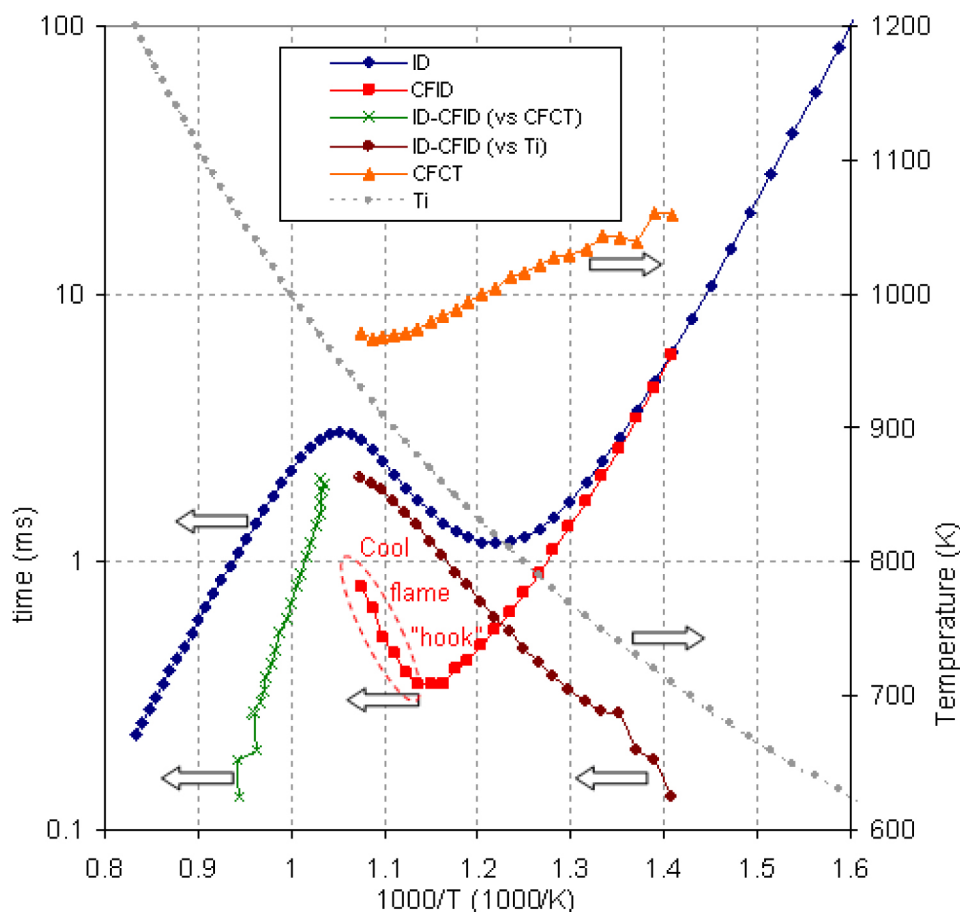


Figure 1. Temperature effects on the auto-ignition of n-heptane; $P=20\text{bar}$; $\Phi=1$; $R=0\%$

- The overall ignition delay (ID) was defined as the elapsed time corresponding to the final peak in the derivative of temperature w.r.t. time for a given fuel.
- The cool flame ceiling temperature (CFCT) was defined as the temperature at the time halfway between the cool flame ignition delay and the overall ignition delay.
- The post cool flame ignition delay (ID - CFID) was defined as the elapsed time between the cool flame event and the main auto-ignition event.

In [Figure 1](#), the post cool flame ignition delay is plotted twice: firstly as a function of the initial temperature as is common in the literature [15,22] and secondly as a function of the cool flame ceiling temperature. The reason for this latter presentation is that the chemistry subsequent to the cool flame is subjected to this ceiling temperature and not the initial temperature. It therefore seems more appropriate to consider the post cool flame ignition delay as a function of the post cool flame temperature. It is acknowledged that the temperature during the post cool flame ignition delay is not constant, but it is considered that this nonetheless represents a better qualitative presentation than the former alternative.

[Figure 1](#) illustrates that the cool flame timing not only deviates from its initial straight-line-Arrhenius behaviour, but also exhibits a region of NTC behaviour before the cool flame heat release magnitude dies away completely. This deviation from the straight-line-Arrhenius behaviour has been observed experimentally for 2-stage fuels in [22;37;42;44;46], but the NTC “hook” in the cool flame timing has seemingly only been observed experimentally in [15]. Perhaps the reason for this sparse experimental evidence of the cool flame NTC hook is highlighted in [52] where the authors state that the cool flame timing appears to follow a straight-line-Arrhenius behaviour but that the CF ID becomes difficult to distinguish and record as the cool flame heat release reduces to low values and merges into the main ignition delay. It is worth noting that this cool flame hook was observed in simulations using both the detailed mechanism from [45] and from [42]. It is therefore believed to be a real and relevant aspect of 2-stage auto-ignition chemical kinetic behaviour.

A careful examination of [Figure 1](#) illustrates the fact that the post cool flame ignition delays vs cool flame ceiling temperature (series shown in green), are significantly shorter than the overall ignition delays (series shown in blue) in the