

# A New Functional Global Auto-ignition Model for Hydrocarbon Fuels - Part 2 of 2: Model Formulation, Development and Performance Assessment

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## 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 second 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).

The formulation of the new functional global auto-ignition model resulted in a computationally efficient model, able to accurately predict heat release dynamics of single and two-stage auto-ignition fuels across a wide range of temperature, pressure, fuel equivalence ratio and inert exhaust product dilution, thereby out-performing the predictive accuracy of currently available global models. The computational efficiency of the new global model out-performed skeletal and reduced chemical kinetic models which may possess similar predictive functionality with regard to 2-stage heat release dynamics.

Although the new functional global model was based on alkane fuel auto-ignition behaviour (iso-octane and n-heptane), it was also shown to fit 1-hexene and a quaternary gasoline surrogate blend without any changes to the model form. Removal of the low temperature chemistry section of the model allowed fitting to methanol and toluene as examples of single stage auto-ignition fuels. This flexibility indicates that the model could be fitted to any hydrocarbon fuel including full boiling range blends. This wide applicability of the new functional global model makes it particularly suitable for HCCI modelling applications.

## 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 2 study sought to utilise the insights and functional requirements developed in the Part 1 study as a basis for formulating a new global auto-ignition model with full single and two-stage heat release predictive capabilities, subject to the effects of pressure, temperature, fuel equivalence ratio and inert exhaust product dilution.

## REVIEW OF FINDINGS FROM PART 1

In Part 1, a detailed fuel auto-ignition behavioural study and analysis of alkane oxidation schematics led to the development of a set of nine functional requirements for the new global auto-ignition model. Existing global auto-ignition models such as the Shell model [22], Müller model [23], Schreiber model [24] and Zheng model [25], were assessed in terms of these requirements and found lacking in various aspects. The requirements are summarised below with reference to the generalised hydrocarbon oxidation chemistry schematic as provided by Zhao et al.[1] and included as [Appendix A](#).

1. The use of least one intermediate species between the fuel species and the reaction/s resulting in low temperature heat release, to control the ignition delay timing. These intermediate species (with reference to [Appendix A](#)) could include alkyl, alkylperoxy, hydroperoxyalkyl, hydroperoxyalkylperoxyl and subsequent alkylhydroperoxide and/or ketohydroperoxide radical pools.
2. A reverse reaction to act on this low temperature intermediate species in a manner which slowed its rate of formation at higher temperature, producing the “cool flame hook”. This slowing of the low temperature chemical pathway could be achieved through the thermal dependencies of the oxygen addition reverse reactions 3 and/or 6 in [Appendix A](#).
3. The cool flame heat release triggering reaction must be strongly dependant on the concentration of the low temperature intermediate species. This reaction rate must, however, also be dependant on temperature to ensure that the low temperature intermediate species does in fact oxidise, even if this concentration is only depleted during the high temperature phase.
4. A reverse reaction activated at an intermediate ceiling temperature to arrest the cool flame heat release. This shutting down of the low temperature chemical pathway could be achieved through the thermal dependencies of the oxygen addition reverse reactions 3 and/or 6 in [Appendix A](#). It was not clear from the outset of the project whether this reverse reaction could be combined with the reverse reaction required in item 2 above. Thermally activated reverse reaction/s would effectively shut down the low temperature reaction path for experiments conducted at high temperature.
5. The use of at least one intermediate species between the fuel species and the reaction/s resulting in high temperature

heat release, to control the ignition delay timing. This species cannot be combined with the low temperature intermediate, since the cool flame arrest reaction would prevent high temperature heat release from occurring. These intermediate species (with reference to [Appendix A](#)) could include hydroperoxy radicals and hydrogen peroxide.

6. The high temperature heat release triggering reaction must be strongly dependant on the concentration of the high temperature intermediate species. This reaction rate must, however, also be dependant on temperature to ensure that the high temperature intermediate species does in fact oxidise, even if this concentration is only depleted near the peak adiabatic flame temperature.
7. The enhanced post cool flame reactivity relative to that exhibited in the high temperature experiments indicates a requirement for enhancing or earlier triggering of the main heat release event where cool flame activity has been present. This enhanced post cool flame reactivity was thought to stem from the post cool flame trapping of hydroperoxyalkyl radicals in the low temperature chemical pathway by the thermal arrest of the second oxygen addition reaction ([reaction 6 in Appendix A](#)) and their subsequent reactions through the alternative reaction path forming alkenes, cyclic ethers and hydroxyl radicals.
8. The use of appropriate dissociation reactions, such as the dissociation of carbon dioxide and/or the “water-gas shift” reaction, in order to prevent over prediction of post combustion temperatures.
9. Reaction rate expressions must incorporate the appropriate coefficients needed to attain sensitivity to the experimental conditions of temperature, pressure, fuel equivalence ratio and inert combustion product dilution. These reaction rate coefficients should be applied only where required in order to attain appropriate agreement without suffering additional model complexity. Apart from temperature sensitivity, these requirements for a given 2-stage auto-ignition fuel are as follows:
  - a. The cool flame ignition delay at low temperature (before the cool flame hook) does not exhibit sensitivity to pressure, equivalence ratio or inert dilution.
  - b. The reverse reaction responsible for the cool-flame hook exhibits sensitivity to pressure, equivalence ratio and inert dilution.
  - c. The cool flame ceiling temperature exhibits sensitivity to pressure, equivalence ratio and inert dilution.
  - d. The post cool flame (enhanced reactivity) ignition delay does not exhibit sensitivity to pressure, equivalence ratio or inert dilution.

e. The high temperature (no prior cool-flame activity) ignition delay exhibits sensitivity to pressure, equivalence ratio and inert dilution.

## MODEL FORMULATION DEVELOPMENT

A key aspect in the approach was to aim for a formulation that allowed direct behavioural adjustment of the model using the reaction rate parameters with the intention that these parameters could then be fitted to data in a direct and robust fashion.

Viljoen et al. [32] used density function theory to examine dominant reaction pathways and made a convincing argument for the hydrogen abstraction of the alkylperoxy radical being the rate determining step in the low temperature chemistry of alkanes (reaction 4 in Appendix A). Other researchers [17, 18, 19] have found that differences in the ignition quality of alkane fuels can largely be addressed by changing the reaction rate parameters of this reaction. This reaction therefore seemed an appropriate choice for controlling the cool flame heat release timing in the new functional global model.

The fact that all four of the models described in the previous section, made no separate provision for the cool flame hook behaviour led to a preliminary suspicion that the achievement of this characteristic might possibly be simultaneously achievable with the cool flame arresting reverse reaction. However, all the preliminary trial models that were formulated to combine the cool flame hook and the cool flame arrest resulted in poor agreement with the detailed simulation data. Models of this form that were tuned to fit the cool flame hook predicted overly high cool flame heat release, while fitting of the cool flame heat release resulted in the cool flame hook shifting to lower temperatures (overly retarded cool flame timing in the intermediate temperature region). It was therefore concluded that these two characteristics would need to be controlled by separate reactions.

According to the schematic in Appendix A, reaction 3 (oxygen addition to form the alkylperoxy radical) is a temperature and pressure sensitive equilibrium reaction, whose forward rate is fast for all temperatures, while the reverse reaction is fast only at high temperatures. This reverse reaction therefore seemed an appropriate choice of reaction for controlling the cool flame hook characteristic.

The only remaining reverse reaction in the low temperature chemistry section of the schematic in Appendix A, was the reverse reaction of reaction 6 - the oxygen addition to form the hydroperoxyalkylperoxyl radical. This reverse reaction was therefore chosen to control the arrest of the cool flame heat release.

The post cool flame enhanced reactivity requirement was regarded as an obvious area of potential improvement for the new global model formulation, especially since the need for this characteristic had been so clearly illustrated in [31] and was conspicuously absent from existing global models [22, 23, 24, 25].

The post cool flame enhanced reactivity was addressed by assuming that the reverse reaction of the schematic's reaction 6 (the cool flame heat release arrest reaction) traps the hydroperoxyalkyl radicals in the low temperature chemical pathway and that the dominant alternative pathway is the decomposition of hydroperoxyalkyl radicals to lighter alkenes or cyclic ethers and hydroxyl radicals. This reaction is represented as reaction 5 in the schematic. It was simultaneously assumed that this reaction is more reactive than reaction 9 (the high temperature chemistry rate limiting reaction) at temperatures typical of the cool flame ceiling temperature. Reaction 5 can only feature in reacting systems that start at relatively low temperatures (below ~800-950K - depending on the fuel) since the reverse reaction 3 blocks the low temperature chemistry pathway for experiments that are started at relatively high temperatures (above ~800-950K - depending on the fuel). The enhanced cool flame reactivity was therefore assumed to be achieved by the trapped hydroperoxyalkyl radicals reacting through reaction 5 and triggering the high temperature chemistry through the enhanced availability of the very reactive hydroxyl radicals.

The heat release of the cool flame and the early stages of the main heat release were assumed to occur through the formation of carbon monoxide, which was assumed to be formed through the decomposition of the alkylhydroperoxide and/or ketohydroperoxide species in the low temperature pathway and hydrogen peroxide in the high temperature pathway. Zhao et al indicated [1] that the decomposition of these species yields the very reactive hydroxyl radicals which in turn undergo rapid chain branching and decomposition reactions to ultimately form carbon monoxide, water and carbon dioxide with the associated significant release of thermal energy. The concentrations of the alkylhydroperoxide/ketohydroperoxide and hydrogen peroxide species were therefore regarded as important in the reaction rates of reactions forming carbon monoxide and water.

The reversible reactions between carbon monoxide and carbon dioxide are temperature dependant such that they only reach fast equilibrium at high temperatures [33]. This means that carbon monoxide formed during the cool flame reaction does not rapidly react further to form carbon dioxide until additional carbon monoxide (and associated heat release) is produced through the high temperature chemistry. This approach was supported by preliminary analysis of species concentrations from detailed chemical kinetic simulations as shown in Figure 1. In this figure label (and subsequent labels)

P refers to the initial 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. The logarithmic concentration scale should be noted with regard to the fact that while carbon dioxide is formed during the cool flame heat release, these concentrations are negligible compared with its later formation during the main heat release.

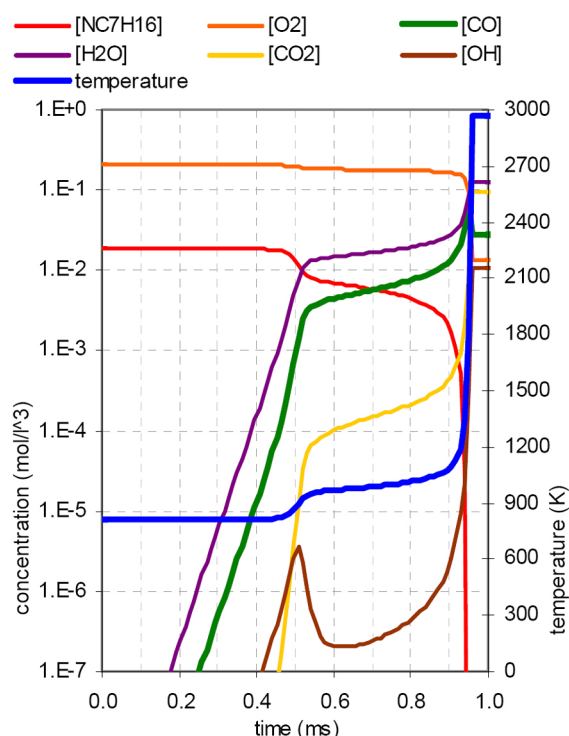


**Figure 1. Temperature and concentrations during the constant volume oxidation of n-heptane at  $T=810\text{K}$ ,  $P=20\text{bar}$ ,  $\phi=1.0$ ,  $R=0\%$ . This detailed kinetic simulation used the mechanism by [34].**

The high temperature chemistry rate limiting reaction is generally agreed [1;34, 35, 36, 37] as being reaction 9 in the schematic - fuel hydrogen abstraction by hydroperoxy radicals to form hydrogen peroxide. This reaction is slow at low temperatures and is also pressure dependant.

The process of development of the new functional global model progressed through several iterations before arriving at a satisfactory formulation. The details of these iterations are dealt with in [38].

## FINAL MODEL FORMULATION

The schematic of the final functional global model formulation is given in Figure 2. In this schematic the letter symbols are representative of species classes as follows:

F: fuel, oxygen and the alkyl radical pool

J: alkylperoxy radical pool

I: hydroperoxyalkyl radical pool

Q: hydroperoxyalkylperoxyl and subsequent alkylhydroperoxide and/or ketohydroperoxide radical pools

Y: hydrogen peroxide, carbonyl radicals, lighter alkenes and ethers

CO: carbon monoxide and water

CO<sub>2</sub>: carbon dioxide

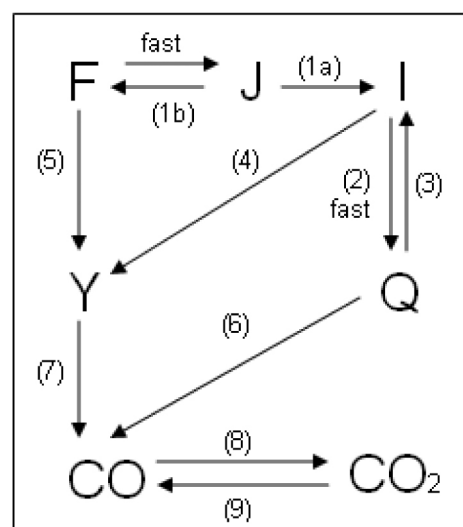


**Figure 2. Schematic of the final formulation for the new functional global model**

This model formulation used the various reactions to fit the alkane kinetic behaviour as follows:

Reaction 1a: the cool flame ignition delay

Reaction 1b: the cool flame hook

Reaction 2: the equivalence ratio effect on cool flame ceiling temperature during the cool flame arrest.

Reaction 3: the cool flame arrest

Reaction 4: the post cool flame ignition delay

Reaction 5: the high temperature ignition delay

Reaction 6: the cool flame heat release

Reaction 7: the first phase of the high temperature heat release

Reaction 8: the second phase of the high temperature heat release

Reaction 9: the control of the adiabatic flame temperature by dissociation effects

Each of the reactions used the conventional Arrhenius form and the reaction sequence from F to J was simplified to a single two-Arrhenius reaction rate descriptor using the quasi-steady-state assumption (QSSA) [11, 12, 13, 14;39]. The reaction rate equations are given in Figure 3 and reaction rate “constant” equations are given in Figure 4.

$$\begin{aligned}
 RR_1 &= 1/(1/K_{1a} + [F]^{a1}[O_2]^{b1}K_{1b}) \\
 RR_2 &= [F]^{a2}[I]^{c2}K_2 \\
 RR_3 &= [Q]^{d3}K_3 \\
 RR_4 &= [I]^{c4}K_4 \\
 RR_5 &= [F]^{a5}[O_2]^{b5}K_5 \\
 RR_6 &= [Q]^{d6}[O_2]^{b6}K_6 \\
 RR_7 &= [Y]^{e7}[O_2]^{b7}K_7 \\
 RR_8 &= [CO]^{f8}[O_2]^{b8}K_8 \\
 RR_9 &= [CO_2]^{g9}K_9
 \end{aligned}$$

**Figure 3. Reaction rate equations for the final functional global model**

$$\begin{aligned}
 K_{1a} &= A_{1a}e^{B_{1a}/T} \\
 K_{1b} &= A_{1b}P^{n_{1b}}e^{B_{1b}/T} \\
 K_2 &= A_2P^{n_2}e^{B_2/T} \\
 K_3 &= A_3e^{B_3/T} \\
 K_4 &= A_4e^{B_4/T} \\
 K_5 &= A_5P^{n_5}e^{B_5/T} \\
 K_6 &= A_6P^{n_6}e^{B_6/T} \\
 K_7 &= A_7P^{n_7}e^{B_7/T} \\
 K_8 &= A_8e^{B_8/T} \\
 K_9 &= A_9e^{B_9/T}
 \end{aligned}$$

**Figure 4. Reaction rate “constant” equations for the final functional global model**

This model formulation exhibited good agreement to a number of 2-stage ignition fuels, through a wide range of temperatures, pressures, fuel equivalence ratios and inert exhaust product dilution.

The challenge of obtaining the correct cool flame ceiling temperature sensitivity to fuel equivalence ratio, while maintaining the correct insensitivity of both the low temperature cool flame ignition delay and the enhanced post cool flame ignition delay to fuel equivalence ratio, was achieved as follows:

1. The insensitive cool flame ignition delay was achieved by making reaction 1a fairly insensitive to fuel concentration.
2. The insensitive enhanced post cool flame ignition delay was achieved by making reaction 4 insensitive to fuel concentration.
3. The sensitivity of the cool flame ceiling temperature to fuel concentration was achieved by making reaction 2 sensitive to fuel concentration. The Arrhenius parameters for this reaction rate were chosen to ensure that this reaction remained faster than reaction 1a, thereby ensuring that reaction 1a (with its negligible fuel concentration sensitivity) remained the rate limiting step determining the low temperature cool flame ignition delay.
4. However, at higher temperatures during the cool flame reaction, the reverse reaction 3 was set up to slow down the low temperature chemical pathway and arrest the cool flame heat release.
5. The effect of reaction 3 during the cool flame arrest therefore changed the rate limiting reaction in the low temperature chemical pathway from the F to I sequence, to the I to Q sequence, thereby bringing into effect the previously ineffective sensitivity of the low temperature pathway to fuel concentration.

It may be argued that this solution is not chemically defensible since reaction 2 essentially represents the internal hydrogen abstraction of hydroperoxyalkylperoxyl to form alkylhydroperoxide and this reaction is unlikely to be directly affected by fuel concentration. There is no good defence against this objection, other than the fact that on the whole, this formulation still remains representative of the basic schematic of alkane oxidation chemistry and the formulation allows excellent agreement between the global model and the numerous behavioural requirements of the detailed chemical kinetic simulation data.