Reduction of a detailed chemical mechanism for a kerosene surrogate via RCCE-CSP

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Abstract

Detailed mechanisms for kerosene surrogate fuels contain hundreds of species and thousands of reactions, indicating a necessity for reduced mechanisms. In this work we employ a framework which combines Rate-Controlled Constrained Equilibrium (RCCE) with Computational Singular Perturbation (CSP) for systematic reduction based on timescale analysis, to reduce a detailed mechanism for a jet fuel surrogate with n-dodecane, methylcyclohexane and m-xylene. Laminar non-premixed flamelets are utilised for the CSP analysis for different strain rates and therefore different scalar dissipation rate, covering the flammable region of strain rates for the surrogate fuel.

Two RCCE-reduced mechanisms are developed via an RCCE-CSP methodology, with 17 and 42 species and their accuracy is assessed in non-premixed flamelets with varying strain rate, in laminar premixed flames for lean, stoichiometric and rich conditions, in igniting flamelets and a flamelet with difference in temperature between fuel and air to test the ignition response and finally in an unsteady non-premixed flamelet with time-dependent strain rate at high pressure and difference frequencies, to test the dynamic behaviour of the RCCE-reduced mechanisms. The profiles of both major and minor species, as well as important combustion characteristics such as ignition strain rate and laminar flame speed, are investigated. The structure of non-premixed flamelets is very well predicted, while the premixed flames are overall well predicted apart from a few deviations and an underprediction in the laminar flame speed. Apart from the large reduction in dimensionality, the reduction in computational time is also considerable (up to 19 times).

As the detailed mechanism comprises 367 species and 1892 reactions, this is

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the first application of RCCE to a mechanism of this size, and the reduced mechanism is validated in non-premixed and premixed laminar flames, in steady-state and also for dynamic response for atmospheric and elevated pressures.

Keywords: kerosene, Surrogate fuels, Mechanism reduction, RCCE, CSP

1 Introduction

Design of jet engines for increased efficiency and reduced emissions is a time-consuming procedure, during which several different configurations and layouts are tested. An experimental approach to this design procedure is costly in terms of both time and resources. In contrast, turbulent combustion CFD with an accurate chemical mechanism provides all the required information for the design process. Benefits from turbulent combustion simulations can impact the efficiency for lower fuel consumption and longer engine life and influence also the reduction of NO\textsubscript{x} emissions and more importantly soot formation, on which stricter restrictions are expected. The challenges in turbulent combustion CFD, however, are the accurate representation of a surrogate fuel, the development of a detailed chemical mechanism and lastly the development of a reduced chemical mechanism in order to incorporate comprehensive chemistry into turbulent combustion CFD. The above mentioned aspects are discussed in the following paragraphs.

1.1 Modelling of surrogate fuels

The most common aviation fuel for aircraft is kerosene, for both transport and military operations. The first challenge in modelling kerosene combustion, however, is the accurate representation of kerosene with a so-called surrogate fuel, as kerosene is a distillate product and therefore includes hundreds of components. These surrogate fuels resemble the most important characteristics of the real fuel, with most of them targeting either the physical properties, like density, viscosity and others, or the fuel’s chemical properties, such as molecular weight and sooting tendency [1].
The first attempts to model kerosene were the early works of Wood et al. [2] who used a 14-component surrogate fuel to model JP-4 (Jet Propellant 4) and Heneghan and Schulz [3] who represented JP-8 with a 12-component fuel; these studies focused on the thermal stability and distillation curve of the real fuels. The pioneering work of Gueret et al. [4] was the first to introduce a surrogate fuel with only three components related to the main hydrocarbon families, namely alkanes, cycloalkanes and aromatics, represented by 79% n-decane, 11% 1,2,4-trimethylbenzene and 10% n-propylbenzene respectively. These components were selected after a chemical analysis of Jet-A1, and the surrogate fuel was later validated in a jet stirred reactor (JSR). No PAHs were included in their compact model with 56 species and 360 reactions, as the fuel was oxidised with global relations straight to C$_4$ species or smaller.

Following these works, Dagaut et al. [5] used a single component surrogate fuel with n-decane to represent kerosene in a JSR at elevated pressures, while Doute et al. [6] used the same surrogate in premixed flames. The similarity observed in [5] was reasonably validated numerically with a detailed mechanism with 90 species and n-decane in [6]. The importance, however, of including an aromatic component in the surrogate fuel to model soot formation in a kerosene flame was also discussed in [7], where 10% toluene was added to 90% n-decane and resulted in reasonable agreement, similar to Maurice et al. [8] who used 78% n-decane and 22% ethylbenzene to predict the CO and NO$_x$ emissions from a well stirred reactor. The work of Lindstedt and Maurice [9] explored the potential of including the aromatic components benzene, toluene, ethylbenzene and ethylbenzene/naphthalene at 11%, accompanied by 89% n-decane as base component of the surrogate fuel, in a mechanism consisting of 193 species and 1085 chemical reactions. Benzene was found to have a disadvantage against the other components, and all the surrogates were compared in the experimental configuration of Doute et al. [6]. Most of these works are covered by the comprehensive review of Edwards and Maurice [1], which also highlights the necessity of multi-component surrogate fuels and the similarity of n-dodecane with kerosene in terms of physical properties. For a historical perspective, Edwards [10] describes the evolution of modelling of liquid fuels, the development of jet engines and the differences in batches of kerosene, along with the physical properties of liquid fuels and the specifications that should be checked.
The work on surrogate fuels, which use n-decane as a main component, was continued by other researchers as well. Dagaut [11] used a surrogate fuel with 74% n-decane, 15% n-propylbenzene and 11% propylcyclohexane, which is different to [4], and developed a detailed mechanism with 207 species to model a JSR under atmospheric pressures and lean and rich conditions. Another modification to [4] was introduced by Honnet et al. [12] to develop the Aachen surrogate fuel with 80% n-decane and 20% trimethylbenzene to predict ignition times, flame speeds and non-premixed flames. Honnet et al. also updated the mechanism from [13], which was initially developed for n-decane combustion, and derived a new one with 122 species. This mechanism was also implemented in a multiphase LES study with Jet-A [14] using non-premixed and premixed flamelets.

Humer et al. [15] developed a detailed mechanism with 283 species and a lumped version with 173 species for testing different surrogate fuels based on different alkanes (n-decane, n-dodecane), different aromatics (o-xylene, toluene) and methylcyclohexane, and concluded that the n-dodecane/o-xylene/methylcyclohexane fuel provided higher accuracy than n-decane/toluene/methylcyclohexane surrogate, while the aromatic component was found not to have significant difference, something that was also noticed by Lindstedt and Maurice [9] for toluene, ethylbenzene and naphthalene. In the same work [15], few more surrogate fuels were also compared in the same configuration including the Drexel surrogate [16], the Utah surrogate [17] and the surrogate fuel developed in [2], which included five, six and twelve components respectively.

The works of Colket et al. [18] and Dagaut and Cathonnet [19] were milestones in the development of jet fuel surrogates. Colket et al. [18] reviewed existing surrogate fuels and compared experimentally the most well-known ones for ignition and extinction along with a new surrogate consisting of 50% n-decane, 25% propyl-benzene and 25% propylcyclohexane, which was also tested at high pressure and lean conditions. Dagaut and Cathonnet [19] reviewed kinetic mechanisms and experimental data for kerosene, highlighting the importance of soot for environmental, military and design reasons and the significant influence of an aromatic component in the surrogate fuel. Regarding the experimental work on surrogate fuels and fuel components, the work of Ranzi et al. [20] reviewed the laminar flame speeds of several hydrocarbon fuels, including large alkanes (n-
decane, n-dodecane), cycloalkanes and aromatics, and provided a database for the components of jet fuel surrogates.

It was only recently [21] that the first systematic method for the development of a surrogate fuel was suggested given specific targets, in this case towards chemical kinetics characteristics including soot tendency; an abstract approach was also attempted in [2]. Dooley et al. [21] suggested a four-component surrogate fuel, developing their previous surrogate fuel [22] to match the combustion properties of kerosene over a wide range of conditions including variable pressure flow reactor, diffusion flames, ignition delay times at high pressure, laminar flame speed and soot volume fractions. Kim et al. [23] developed two surrogate fuels using a systematic method similar to [21], but targeting the physical properties of kerosene; they studied the influence of different cycloalkanes comparing methylcyclohexane and decalin and the surrogate fuels were found to reproduce most of physical and chemical properties under examination. Narayanaswamy and co-workers also identified the necessity of a systematic way for the development of a surrogate fuel and introduced a methodology to select the composition of the surrogate components through an optimisation of specific targets, in this case for the chemical representation of the real fuel [24]. Most of the above mentioned surrogate fuels are shown in the following Table 1.

As briefly described in the previous paragraphs and also in [18], research still needs to be undertaken in the field of surrogate fuels in order to conclude to targets to be used for improved design of jet engines and reduced emissions. Systematic methods are indeed the only solution to the problem of identifying the composition of the surrogate fuel, but no suggestions exist for selecting the number of components in the surrogate fuel to represent the different hydrocarbon families and which components should be selected.

1.2 Detailed mechanisms

Some of the pioneering works regarding the development of surrogate fuels and detailed chemical mechanisms were discussed in the previous paragraph, while here some works that suggested only kinetics for known surrogates are reviewed. Patterson et al. [26] used a chemical mechanism including parts of GRI mechanism
Table 1: Composition (%) of available surrogate fuels.

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and others, with 85 species and 440 chemical reactions. This mechanism was validated in a JSR configuration and in premixed flames (compared with the results from [6]) and non-premixed flames at high strain rates, using the surrogate fuel from Lindstedt and Maurice [9]. The surrogate fuel from [17] was used in [27].

A detailed mechanism for the oxidation of n-dodecane was suggested in [28] and tested for burning velocities, ignition times and pyrolysis. The mechanism was based on USC Mech-II with an addition of 60 species, containing 171 species and 1306 reactions, and was found to predict accurately combustion characteristics. The additional set for the description of C₅-C₁₂ combustion was then simplified and described with 4 species only and 20 steps, leading to accurate prediction of burning velocities and ignition delay times above 1100 K and moderate performance regarding species concentrations; this simplification, however, indicates the ability to decouple the C₅-C₁₂ chemistry to describe fuel cracking. Narayanaswamy and co-workers [29], [30], [31], [24] developed a kinetic library including the necessary kinetics for a wide range of hydrocarbons that are required for surrogate modelling and soot kinetics. The mechanism that they derived has been widely tested in all combustion regimes for ignition delay times, flame speeds, extinction rates and species profiles showing good agreement with experimental data, and is the starting mechanism employed for reduction in this work.

1.3 Reduced mechanisms

While detailed mechanisms for kerosene surrogates provide good results for a wide range of problems, CFD simulations of real problems with such mechanisms are computationally infeasible. The detailed mechanisms for jet fuels described in the previous paragraph may easily contain hundreds of species and thousands of reactions, indicating a necessity for reduced mechanisms.

Few studies developing reduced chemical mechanisms for jet fuel surrogates exist in the literature. Kyne et al. [32] developed a chemical mechanism with 84 species and 440 reactions for the prediction of a premixed flame [6], using the surrogate fuel suggested in [9] with 89% n-decane and 11% toluene. Using sensitivity and reaction rate analysis to simplify 24 species, this is, to our knowledge, the only work on reduced mechanisms which studied profiles of aromatic and interme-
diate species. CARM [33] was then utilised by Montgomery et al. [25] to derive several reduced mechanisms with a limit at 20 species, mainly for implementation in CFD. The reduced models were based on a a modification of a detailed mechanism [5], with a simplified surrogate with 34.7% n-decane, 32.6% n-dodecane, 16% butylbenzene and 16.7% methycyclohexane for JP-8, and they were validated only for some major products in perfectly stirred reactors (PSR), without concluding to a global set, but instead providing several reduced mechanisms for different conditions.

Systematic methods were also used in other works to develop reduced mechanisms; Luche et al [34] used atomic flux and principal component analysis (PCA) on a three-component surrogate fuel mechanism [11] to derive two schemes with 33 and 40 species, which were tested in JSR with good results. The last stage of reduction was under the criterion that target major species, such as fuel components, CO₂, CO, O₂ and others should have a relative error below 10% in the reduced mechanism. A sensitivity analysis followed by an iterative lumping procedure using several validation cases for ignition times and burning velocities was used by Slavinskaya [35], who developed a reduced mechanism with 40 species. The resulting mechanism with a surrogate fuel consisting of 12% n-heptane, 23% iso-octane and 65% n-decane performed well in the PSR compared to real jet fuel.

Zetervall et al. [36] developed a semi-global reduced mechanism using n-dodecane as a single surrogate fuel and only few steps to describe its breakdown directly to C₂ species, with all the intermediates discarded. This 22-species mechanism predicts accurately laminar burning velocities, major product species, extinction rates and some radicals, but fails to predict ignition times and C₂ species, obtaining however impressive speed-up in computational time. Other recent attempts to provide reduced mechanisms for kerosene surrogates using the fuel from [11] and a 34-species reduced mechanism through a combination of sensitivity analysis, flux analysis, QSSA and CEMA can be found in [37], while only recently [38], a slightly modified surrogate based on n-decane was accompanied by a 59-species reduced mechanism after DRGEP [39], PCA, path flux analysis and an optimisation procedure [40] and was finally tested in a PSR. DRGEP with an additional sensitivity analysis were also used in [41] to reduce a detailed mechanism [42] for n-decane from 2115 species to a high temperature 51 species mechanism, which reproduced
accurately the ignition times, while laminar flame speeds and PSR results exhibited a small error. Lastly, Franzelli et al. [43] introduced a two-step chemistry mechanism with 5 species and the fuel $C_{9.7396}H_{20.0542}$.

1.4 Objectives

The objectives of this work are mainly three. Firstly, two reduced chemical mechanisms are derived for a jet fuel surrogate, as only few reduced mechanisms for different surrogate fuels for kerosene exist in the literature. These mechanisms are obtained via a methodology based on Rate-Controlled Constrained Equilibrium (RCCE) and Computational Singular Perturbation (CSP), which was recently developed by the authors [44]. The essence of the methodology is to investigate the timescale separation via CSP over a range of conditions generated through laminar non-premixed flamelets covering the flammable part of strain rates and to determine a global set of slow or kinetically-controlled species to be employed in RCCE. Secondly, three new problems for RCCE are employed in this work, namely: high pressure flamelets, unsteady non-premixed flamelets with time-depending strain rate and the igniting flamelets with hot air products. Lastly, and most importantly, the objective and motivation of this work is to test the limits of the RCCE-CSP methodology derived in our group [44]. This is achieved via the reduction of the detailed mechanism from [24] with 367 species and 1892 reactions for a surrogate fuel with n-dodecane, methylcyclohexane and m-xylene. In this way, not only we explore the limits of the RCCE-CSP methodology, but also the limits of RCCE itself, as this is the first time that such a degree of reduction is deemed.

The RCCE-reduced mechanisms are validated in non-premixed flamelets, premixed flames, igniting flamelets and an unsteady flamelet; the last two cases are employed for assessing the dynamic response of the mechanisms. Considerable degree of reduction is obtained reducing the CPU time up to 19 times compared to the full model, while maintaining the accuracy of major species and radicals’ profiles, such as CO, CO$_2$, fuel components, C$_2$H$_2$, OH and H. It must be stressed that an extended comparison for many species profiles exists in this work on top of major product species.

The RCCE-CSP synergy is briefly summarised in Sec. 2, followed by the pro-
cedure of developing the two RCCE-reduced mechanisms and a discussion of their performance. The validation of the reduced mechanisms in the model problems is presented in Sec. 4 followed by conclusions.

2 Methodology of deriving RCCE-reduced mechanisms via CSP

Mechanism reduction exploiting the separation of timescales has traditionally been based on the Quasi-Steady State Approximation (QSSA) and Partial Equilibrium (PE) concepts, and methods for developing reduced mechanisms have been reviewed by [45], [46]. RCCE is an alternative concept, originally proposed by Keck and Gillespie [47] and later re-formulated as a mechanism reduction method and applied to laminar and turbulent flames in [48], [49], [50], [51], [52], [53]. Like QSSA and PE, RCCE yields the reduced system for a given selection of species to be retained. The choice of these species must be based either on heuristics or on a systematic investigation of the timescales. Recent work by the authors [44] has proposed a methodology for combining RCCE with CSP, the latter providing the selection of the leading species. What follows is a summary of the basic ideas involved.

2.1 Rate Controlled Constrained Equilibrium

Similar to QSSA and PE, RCCE is based on the concept of time scales separation; this implies that a number of species evolve according to faster time scales than the rest and reach an equilibrium state constrained by the slow species. Therefore it should be possible to obtain the concentrations of these species by minimising an energy function. It must be emphasised that the entire chemical system is not in equilibrium, and its evolution is still determined by the kinetics of the slow species. We adopt the terminology of [44] and refer to the slow species as kinetically controlled species and to the fast species as equilibrated.

The energy function to be minimised is called the *kinetically constrained energy* [44]. This function depends on the imposed constraints, and therefore on the choice of kinetically controlled species. Consequently this selection must be such
that time scales separation is indeed present between the kinetically controlled and equilibrated species. This is akin to QSSA and PE, whose validity depends on the choice of quasi-steady state species and equilibrated reactions respectively. The role of CSP in the methodology is to provide this selection in a systematic way.

In order to summarise the RCCE equations, let us first write the set of equations describing the detailed kinetics for a chemical reaction mechanism featuring $N_e$ atomic elements, $N_s$ species and $N_r$ reactions. The dynamical evolution is described by a set of differential equations in terms of the reaction rates of individual reactions, $r_k$, and the stoichiometric factors, $\nu_{jk}$:

$$\frac{dn_j}{dt} = \sum_{k=1}^{N_r} \nu_{jk} r_k(n_1, \ldots, n_{N_s}, T, \rho) \quad (j = 1, \ldots, N_s) \quad (1)$$

solved together with the algebraic equations:

$$\sum_{j=1}^{N_s} n_j h^o_j(T) = h \quad (2)$$

$$\sum_{j=1}^{N_s} n_j \rho RT = p \quad (3)$$

Here $n_j$ denotes the concentrations of chemical species in kmol per unit mass of the mixture, a notation especially suited to variable density gas flows, while $h$ is the specific enthalpy of the mixture and $h^o_j(T)$ is the specific enthalpy of each species (both formation and thermal) and $p$ is the total pressure.

The dynamical evolution of the chemical system in RCCE is calculated by combining the differential equations of chemical kinetics with the algebraic equations defining the constrained equilibrium manifold, which are derived by minimisation of the kinetically constrained energy function. A detailed derivation can be found in [44]. The final equations for the evolution of kinetically controlled species and
for the composition at the constrained equilibrium state are respectively:

\[
\frac{dC_i}{dt} = \sum_{j=1}^{N_s} a_{ij}^{c} \sum_{k=1}^{N_r} \nu_{jk} r_k \quad (i = 1, \ldots, N_c) \quad (4)
\]

\[
n_j = n \frac{p_o}{p_j} \exp\left(\frac{-\mu_j^0}{RT}\right) - \sum_{i=1}^{N_e} a_{ij}^e L_i^e - \sum_{i=1}^{N_c} a_{ij}^c L_i^c \quad (j = 1, \ldots, N_s) \quad (5)
\]

where \(\mu_j^0\) is the chemical potential of pure species in a standard state of pressure \(p_o\), \(p_j\) the partial pressure, given by the ideal gas law, \(a_{ij}^e\) is the elements matrix, \(C_i\) are the kinetically controlled species and \(a_{ij}^c\) is a matrix defining the kinetically controlled species. The factors \(L_i^e\) and \(L_i^c\) are the Lagrange multipliers employed for the minimisation of kinetically constrained energy associated with the elements and kinetically controlled species respectively, scaled by the factor \(-1/RT\). This set of equations ensures that the system remains always on the constrained equilibrium manifold. These ODEs must be solved together with algebraic equations expressing conservation of elements and enthalpy and the ideal gas law. These equations form a differential-algebraic (DAE) problem, the dependent variables being the species, element, constrained potentials, temperature and density. In order to obtain initial conditions for the potentials, the constrained equilibrium algebraic equations must be solved for the initial state.

It must be emphasised that the equations of RCCE describe an arbitrary reduced mechanism where the selection of kinetically controlled and equilibrated species enters the formulation only as a parameter, via the entries in the matrix \(a_{ij}^c\). This fact greatly facilitates the investigation of different reduced mechanisms.

### 2.2 Selection of kinetically controlled species

CSP [54], [55] is a widely employed method for developing reduced mechanisms in a systematic way and it has been employed for the derivation of QSSA mechanisms based on laminar premixed flames [56]. In [44] it was proposed to perform the CSP analysis on laminar non-premixed flamelets in order to select the kinetically controlled species in RCCE and the main from this work [44] are summarised
According to the CSP theory, if there exists a separation of timescales, then the $M$ fast and the $R = N_s - M$ slow modes are decoupled and the species which are related to these slow modes are ideal candidates to be the kinetically controlled species in RCCE. Therefore, the number of species to be retained in the reduced mechanism is related to the number of slow modes and, in this work, this number $R$ is defined by the user. In order to associate the slow modes with the major species, the radical pointer [55] is employed with contribution only from the $R$ slowest modes:

$$D_i = \sum_{j=R}^{N_s} \alpha_{ij} b_{ji} \quad (i = 1, ..., N_s)$$  \hspace{1cm} (6)

The species that are related to the slow modes are identified as those exhibiting higher $D_i$ indices and are good candidates for constraints in RCCE. The final pointer, which is different to the one employed in [56], takes into account the concentration of each species, similar to the criterion developed from Peters and Kee [57] and also in the recent work of Jaouen et al. [58]:

$$P_i = D_i y_i \quad (i = 1, ..., N_s)$$  \hspace{1cm} (7)

where $y_i$ is the mass fraction of each species.

This analysis is valid for a local composition only. In order to obtain a global set of constrained species, an investigation based on a set of non-premixed flamelets is conducted. The flamelet equation in mixture fraction space is employed [59]:

$$\rho \frac{\partial n_j}{\partial t} = \rho \chi(z) \frac{\partial^2 n_j}{\partial z^2} + \dot{\omega}_j$$  \hspace{1cm} (8)

where $z$ is the mixture fraction and $\chi$ is the scalar dissipation rate, given in terms of the strain rate, $S$, as follows:

$$\chi(z) = \frac{S}{\pi} e^{-2[erf^{-1}(2z)]^2} \quad (z = 0, ..., 1)$$  \hspace{1cm} (9)

The local pointer $P_i$ is then integrated across the flammable part of the mixture.
fraction space to obtain a local ordering for each strain rate, $S_s$:

$$P_i^s = \int_{z_l}^{z_r} P_i dz \quad (i = 1, ..., N_s)$$  \hspace{1cm} (10)

where $z_l$ and $z_r$ are the lean and rich flammable mixture fractions. This means that the species with large mass fractions, which are also associated with the slow subspace and slow modes (high $D_i$ indices), will be highest ranked and will be the first to be constrained in RCCE.

The final ordering results from weighting the $N_{st}$ local integrated CSP pointers between the two extinguishing strain rates to account for the different parts of composition space accessed, when modifying the strain rate. This yields:

$$P_{i}^{glob} = \sum_{s=1}^{N_{st}} P_i^s (1 - \frac{|S_s - S_m|}{S_m}) \quad (i = 1, ..., N_s)$$  \hspace{1cm} (11)

where $S_m$ is the mean flammable strain rate. The weighting of the pointers for each strain rate provides then the global set of species.

3 Development of a reduced mechanism

3.1 Detailed mechanism

The detailed mechanism that will be used as the starting point for this work is due to Narayanaswamy and co-workers, and it has been developed on the basis of a previously derived detailed mechanism [60] with additional studies for different components of the surrogate fuel including aromatic species [29], n-dodecane [30] and methylcyclohexane [31]. The chemical mechanism consists of 1892 chemical reactions between 367 species. Very recently, the same group suggested a surrogate fuel for kerosene which relies on a systematic selection of the components to match the following combustion properties of kerosene: 1) the heating value through the H/C ratio, 2) the molecular weight through carbon and hydrogen number, 3) reactivity through cetane number and 4) sooting tendency through a threshold sooting index. The three selected components to represent the paraffins, cycloparaffins and aromatics of the fuel are n-dodecane, methylcyclohexane and
m-xylene respectively; a rationale for the selection of the specific components can be found in [24]. N-dodecane and methylcyclohexane have widely been used from other researchers as well, either as single component surrogate [61] or in surrogates with multiple components [16] [17] [23], while m-xylene had not been explored as an aromatic representative. The details of the surrogate fuel are shown in Table 2.

<table>
<thead>
<tr>
<th>Property</th>
<th>Kerosene (JP-8, Jet A/A-1)</th>
<th>Surrogate Fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>H/C ratio</td>
<td>1.91</td>
<td>1.92</td>
</tr>
<tr>
<td>av. chem. formula</td>
<td>C_{11}H_{21}</td>
<td>C_{8.73}H_{16.79}</td>
</tr>
<tr>
<td>molecular weight</td>
<td>153</td>
<td>121.8</td>
</tr>
<tr>
<td>composition (% volume)</td>
<td>60% n- &amp; iso-paraffins</td>
<td>44.0% n-dodecane</td>
</tr>
<tr>
<td></td>
<td>20% cycloparaffins</td>
<td>39.4% methylcyclohexane</td>
</tr>
<tr>
<td></td>
<td>18% aromatics</td>
<td>16.6% m-xylene</td>
</tr>
<tr>
<td></td>
<td>2% other</td>
<td></td>
</tr>
</tbody>
</table>

This mechanism and surrogate fuel was widely tested [24] against available experimental data for ignition delay times for wide range of temperatures, pressures and equivalence ratios, for laminar flame speeds at different conditions, for profiles of major species in shock tubes and the data from the premixed flame of Doute et al. [6]. In all examined configurations, the pair of mechanism and surrogate fuel exhibited an overall good performance.

### 3.2 Selection of constraints

Several sets with varying number of kinetically controlled species were derived using the methodology described in Sec. 2.2. The sets were initially tested for a few important cases, before selecting two sets for a comprehensive investigation. These sets were chosen so that the first one is the smallest set able to reproduce the basic features of kerosene surrogate combustion, while the second one retained enough species to approximate closely the detailed mechanism.
The first test was the ability to predict the extinction limit of a non-premixed flamelet for increasing strain rate. Successive flamelets were calculated with strain rate ranging from very low up to the extinction limit, which is between $800 \text{ s}^{-1}$ and $900 \text{ s}^{-1}$, for atmospheric pressure and temperature $T_u = 400$ K for both fuel and air, while the mixture was initialised from equilibrium composition for each strain rate.

Eleven reduced sets containing 15-44 species are shown in Fig. 1, where it is obvious that there are three distinct groups. The smallest set with 15 kinetically controlled species extinguishes even at the very low strain rates, indicating that a bigger set is required. The second group includes RCPK17 (RCCE-CSP mechanism for kerosene with 17 kinetically controlled species) and several sets including up to 32 species. All these sets extinguish between strain rates $500 \text{ s}^{-1}$ and $600 \text{ s}^{-1}$, while the detailed mechanism extinguishes at higher strain rates. Finally, a third group includes the sets with 35-42 species, where the flammable range is extended to higher strain rates. The biggest of these sets, RCPK42, is the smallest set that can predict the extinction limit and further increasing the number of kinetically controlled species has no influence. The smallest set that provided reasonable performance up to intermediate strain rates is RCPK17. An additional constraint in both reduced mechanisms is the total number of moles, which was found to make an improvement in the laminar flame speed, though the difference was small in most of the species’ profiles. While this was not necessary in our previous reduction of methane and propane chemistry [44], this is likely to be due to the fact that the number of species constrained here are a much smaller percentage of the total number of species than in the case of methane and propane (about 52% for CH$_4$, 24% for C$_3$H$_8$ as compared with 5% for RCPK17 and 11% for RCPK42), in order to keep the size of the reduced mechanism manageable.
Figure 1: Peak temperature for several RCCE reduced mechanisms against the detailed mechanism (red dashed line) for a laminar flamelets with varying strain rate at $p=1$ atm and $T_u = 400K$. 
In order to quantify the performance of each RCCE-reduced mechanism, some additional targets were set. These targets included the accuracy in predicting temperature, C$_2$H$_2$ (which is an important species for soot formation) and CO. The performance of several sets is shown in the following figures for CO, C$_2$H$_2$ and temperature for strain rate 500 s$^{-1}$, which is the highest flammable strain rate for the smaller set RCPK17.

Firstly, the temperature at this strain rate is examined, as an overall characteristic. The trend is well captured even with the smallest set RCPK17. It is only until we constrain more than double the number of species, namely in RCPK35, that significant improvement in accuracy is obtained. Slightly better results are achieved until we constrain 42 species, where the accuracy is very good.

Secondly, several reduced sets are compared to the detailed mechanism for target species CO (Fig. 3) and C$_2$H$_2$ (Fig. 4). Regarding CO, the difference between the reduced sets is now more pronounced: all the sets with 17-40 species

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2Similar accuracy is observed for the whole set of strain rates studied.
exhibit similar performance, while the sets from 42-70 species have identical results. In the prediction of C\textsubscript{2}H\textsubscript{2}, the improvement in accuracy occurs between the sets featuring 35 and 40 species; the sets with 17-35 species constantly overpredict C\textsubscript{2}H\textsubscript{2} while the sets with 40-70 species show very good agreement.

Figure 3: CO profiles for several reduced mechanisms against the detailed mechanism (red dashed line) for varying number of kinetically controlled species at p=1 atm, s = 500 s\textsuperscript{-1} and T\textsubscript{u}=400K.
The CPU time corresponding to each mechanism is shown in Fig. 5 for the same case at p=1 atm, $s = 500 \text{ s}^{-1}$ and $T_u=400\text{ K}$. The smallest mechanism (RCPK17) is about 19 times faster than the detailed mechanism. As the number of kinetically controlled species is increased, the speedup is reduced, leading to RCPK40, RCPK42 and RCPK50 that are about 6-8 times faster than the detailed mechanism. While RCPK17 is not very accurate, its compact size and lower CPU time requirements could be beneficial for repeated simulations. On the other hand, RCPK42 would be a good choice if higher accuracy is required, while the CPU savings are still considerable.
Overall, the following conclusions can be drawn from the above described investigation. First, there is a significant increase in accuracy for the RCCE-reduced mechanism RCPK42 compared to the smaller sets. Second and more important, that there is no significant improvement of the performance of the reduced mechanisms when species are added on the RCPK17 up to RCPK42 and from RCPK42 to RCPK70. Therefore the remaining of this work will focus on the investigation of these two sets, the first of which combines small size with reasonable agreement with the detailed model, while the second one attains much higher accuracy while still maintaining a manageable size.

The mechanisms shown in Fig. 1 and discussed above are listed in Table 3, with their names in the detailed mechanism and with their chemical formulas. Regarding RCPK17, most of the well known major species are retained in the mechanism; these are the three surrogate components n-dodecane, m-xylene and methylcyclohexane, the major products CO, CO$_2$, H$_2$O, H$_2$ and O$_2$, as well as OH. The methodology also identifies some important species which are indeed needed
for soot modelling like acetylene, the aromatics pyrene (C_{16}H_{10}), benzene and ace-
naphthylene (C_{12}H_{8}). Most of the small-to-large hydrocarbon range is represented
in the mechanism, except from the C_3 and C_4 section. RCPK42 has a much bet-
ter representation of most of the intermediates including some C_3 and C_4 species
such as propylene (C_3H_6), propargyl radical (C_3H_3), butadiyne (C_4H_2), propyne
(p − C_3H_4), allene (a−C_3H_4) and butadiene (C_4H_6). In addition to this, more
aromatic species are retained in the mechanism, including toluene (C_7H_8), naph-
thalene (C_{10}H_8), phenanthrene (C_{14}H_{10}) and xylyl radical (C_8H_9), which makes
RCPK42 more suitable to couple with soot models. Some additional important
species maintained in RCPK42 include the methyl radical CH_3 and hydrogen atom
H, as well as acetaldehyde which is the only C-H-O species. For completion,
the next species which would be included after the first 42 are acephenanthrene
(C_{12}H_{10}) and ethylbenzene (C_8H_{10}).

Even though a direct comparison with other reduced mechanisms is not real-
istic due to different surrogate fuels and different detailed models, a closer look at
the retained species is helpful. Montgomery et al. [25], included propylene (C_3H_6)
in all six of their CARM-developed sets on top of the four surrogate components.
In the reduced mechanisms with 20 species, they also used more intermediate hy-
drocarbons compared to the smaller ones, some of which being benzene, propyne
(p−C_3H_4) and styrene (C_8H_8). Using again n-decane as the basis for the sur-
rogate fuel along with propylbenzene and propylcyclohexane initially developed
from Gueret et al. [4], Luche et al. [34] also included toluene, benzene and other
hydrocarbons to cover the whole range, providing however results only for the
small hydrocarbons and major products. The 40-species reduced mechanism from
Slavinskaya [35] for a surrogate with toluene, iso-octane and n-decane covered
the range of hydrocarbons quite well, including several intermediate hydrocarbons
from the C_3 - C_{10} family, and predicted ignition delay times but no species’ profiles
were presented. The very recent mechanism from Zettervall et al. [36] included
only few global steps for the transition from the n-dodecane surrogate to C_2 species.
Table 3: Ordering of species for RCCE-reduced mechanisms with 17 and 42 kinetically controlled species.

<table>
<thead>
<tr>
<th>Species name</th>
<th>RCPK17</th>
<th>RCPK42</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 CO₂</td>
<td>18 C₃H₆</td>
<td>29 C₁₄H₈</td>
</tr>
<tr>
<td>2 H₂O</td>
<td>19 C₁₂H₈</td>
<td>30 C₆H₁₀</td>
</tr>
<tr>
<td>3 CO</td>
<td>20 C₁₀H₈</td>
<td>31 C₇H₁₂</td>
</tr>
<tr>
<td>4 O₂</td>
<td>21 C₆H₆</td>
<td>32 C₁₁H₁₀</td>
</tr>
<tr>
<td>5 C₂H₂</td>
<td>22 C₃H₃</td>
<td>33 CH₃</td>
</tr>
<tr>
<td>6 C₁₆H₁₀ A₄</td>
<td>23 C₃H₂</td>
<td>34 H</td>
</tr>
<tr>
<td>7 C₂H₄</td>
<td>24 C₁₄H₁₀ A₃</td>
<td>35 C₅H₇</td>
</tr>
<tr>
<td>8 CH₄</td>
<td>25 C₁₂H₈ A₂C₂HA</td>
<td>36 C₄H₂</td>
</tr>
<tr>
<td>9 n-C₁₂H₂₆</td>
<td>26 C₇H₈ A₁CH₃</td>
<td>37 C₁₂H₁₀ P₂</td>
</tr>
<tr>
<td>10 C₇H₁₄ mch-C₇H₁₄</td>
<td>27 p-C₃H₄</td>
<td>38 C₃H₆</td>
</tr>
<tr>
<td>11 C₆H₆ A₁</td>
<td>28 C₁₆H₁₀ FLTN</td>
<td>39 C₄H₄</td>
</tr>
<tr>
<td>12 H₂</td>
<td>29 C₁₄H₈ A₂R₅C₂H</td>
<td>40 C₃H₉ A₁CH₅CH₂</td>
</tr>
<tr>
<td>13 OH</td>
<td>30 C₆H₁₀ x₁₃C₆H₁₀</td>
<td>41 a-C₃H₄</td>
</tr>
<tr>
<td>14 C₁₈H₁₀ A₄R₅</td>
<td>31 C₇H₁₂</td>
<td>42 C₃H₄O CH₃CHCO</td>
</tr>
<tr>
<td>15 C₅H₁₀ A₁CH₃CH₃</td>
<td>32 C₁₁H₁₀ A₂CH₃</td>
<td></td>
</tr>
</tbody>
</table>
4 Validation of reduced mechanisms

Following the selection procedure, the two RCCE-reduced mechanisms that were selected, one for efficiency and compact size (RCPK17) and one for accuracy (RCPK42), are thoroughly tested here in several problems. These problems are: the non-premixed laminar flamelet (the same combustion regime from which the mechanisms are derived), laminar premixed flames and dynamics in non-premixed flames. The first dynamical problem is the igniting flamelet, where a flamelet is ignited only within a small pilot close to stoichiometry, instead of being initialised with equilibrium composition; in this way, the mixture fractions which are close to stoichiometry and initially unburnt experience a large gradient in temperature and ignition phenomena can be studied. The second dynamical problem is an unsteady non-premixed flamelet with time-dependent strain rate, where we can see the dynamic response of the mechanisms to an imposed periodic variation of the strain rate. Finally, ignition is also studied in a non-premixed flamelet with hot air stream.

4.1 Laminar flamelet

A direct comparison of the two reduced mechanisms with the detailed mechanism is shown in Figs. 6 and 7, for two different conditions: at lower strain rate $s = 200 \text{s}^{-1}$ and at a higher $s = 500 \text{s}^{-1}$, with the second one being close to the extinction limit of the smaller mechanism RCPK17. Regarding the lower strain rate, the accuracy achieved with the two mechanisms is remarkable, even for some radicals such as OH. Specifically for CO, however, there is a difference between the two RCCE-reduced mechanisms with the larger RCPK42 predicting this target species with a maximum error of 2% at low strain rate and an overall error below 1%. A special note must be taken about the performance of the mechanisms in predicting species which are important for soot formation, such as acetylene ($\text{C}_2\text{H}_2$). Looking at Fig. 6, RCPK42 predicts acetylene with an overall error below 2%, while RCPK17 predicts the trend but with an overall overprediction with maximum local error around 30% close to stoichiometry.

A similar behaviour is obtained at higher strain rates Fig. 7, where the chem-
ical phenomena are more complex, and the two mechanisms perform well in the prediction of major species like CO$_2$, H$_2$O and temperature as well as radicals such as OH. Here, again the smaller RCPK17 has a small error (around 10%) in predicting CO and both mechanisms predict similar profiles for acetylene. At the higher strain rate ($s = 800$ s$^{-1}$) RCPK42 exhibits similar performance as at the two strain rates shown, hence results for that are not shown. Overall, the two reduced mechanisms provide similar profiles for major species such as CO$_2$, H$_2$O, H$_2$, OH and temperature for varying strain rate, while RCPK42 exhibits higher accuracy for CO and acetylene.

Both mechanisms are also validated at higher pressure $P = 12$atm in Fig. 8; again good predictions are obtained, with the error remaining below 1% for most of the species profiles, except for CO (5%), H$_2$ (10%) and C$_2$H$_2$ (5%) with RCPK17 and H$_2$ (8%) for RCPK42. The results for higher pressure imply that the reduced mechanisms are good candidates for application in realistic conditions for jet engines.
Figure 6: Comparison of species’ profiles with RCPK17 (blue dashed lines), RCPK42 (blue solid lines) and detailed mechanism (red circles) for a laminar flamelet at $s = 200 \, \text{s}^{-1}$, $p=1 \, \text{atm}$ and $T_u = 400 \, \text{K}$. 
Figure 7: Comparison of species’ profiles with RCPK17 (blue dashed lines), RCPK42 (blue solid lines) and detailed mechanism (red circles) for a laminar flamelet at $s = 500$ s$^{-1}$, $p=1$ atm and $T_u = 400$ K.
Figure 8: Comparison of species’ profiles with RCPK17 (blue dashed lines), RCPK42 (blue solid lines) and detailed mechanism (red circles) for a laminar flamelet at $s = 400 \text{ s}^{-1}$, $p=12 \text{ atm}$ and $T_u = 400 \text{ K}$.

4.2 Premixed flames

Having derived and tested the RCCE-reduced mechanisms in non-premixed flamelets, RCPK17 and RCPK42 are here tested in a one-dimensional laminar premixed flame. Three different conditions were examined, across the whole range of equivalence ratios, at atmospheric pressure and $T_u = 473 \text{ K}$, while results include species profiles and burning velocities for all cases. Results are shown in Figs. 9 - 11, and both mechanisms exhibit an overall good agreement compared to the full mechanism for the temperature profiles as well as for the major species. Regarding the temperature and major product species $\text{CO}_2$, $\text{CO}$, both RCPK17 and RCPK42
exhibit similar response with good predictions in all lean, stoichiometric and rich conditions, with RCPK42 showing an overall better representation of CO inside the flame region. The products H$_2$O, OH and H$_2$ are also well followed from both mechanisms with the average error between 5% and 10%, except of the H$_2$ profile in the lean equivalence ratio with RCPK42 exhibiting an average error of 20% and RCPK17 25%, which is however reasonably reproduced by RCPK42 at stoichiometric and very well at rich conditions. A deviation of the order of 10% in the RCPK17 predictions for OH at all equivalence ratios can also be observed at the flame and burnt region, while H$_2$O is accurately reproduced by RCPK42 but exhibits a small error in RCPK17. Here it must be stressed that only the 50% of the domain is plotted, to magnify the differences very close to the flame region.

The last case for which the RCCE-reduced models are examined is a stoichiometric premixed flame at higher pressure $P = 12$ atm. The accuracy of both mechanisms is good, with smaller errors than in the atmospheric pressure cases. Looking at the surrogate components, RCPK17 predicts a slightly wider flame region, something which can be observed in all three cases but mainly in the lean flame, Fig. 9, while RCPK42 predicts all three components at all mixture fractions with an overall error below 1%.

The laminar flame speed for the reduced mechanisms is compared against the full model in Fig. 13, for a laminar premixed flame at atmospheric pressure and $T_u = 473$ K. The results are reasonably good, particularly for RCPK42, but there is an overall underprediction. This underprediction could be explained by the large degree of reduction employed in these mechanisms. The addition of the total moles improved the agreement in laminar flame speeds by about 10% without the need to add many more species. It must be mentioned that, while there are global mechanisms with only a few steps that reproduce the laminar flame speed accurately, such mechanisms are produced by having the kinetics calibrated to do this, using steady laminar flame data. In RCCE the kinetic data of the detailed elementary mechanism is unchanged; reduction is based purely on time-scale separation imposed via the concept of constrained equilibrium, while all the original reactions and kinetics pertaining to the major species are entirely unmodified. The only parameter is the choice of constrained species, which is also fixed here in order to be rigorously based on the investigation of time scale
separation via CSP. It would be far more flexible to predict parameters such as the laminar flame speed if modification of the kinetics of reactions was allowed, but this is not permitted in the context of the methodology presented here.

The dependence of laminar flame speed on increasing pressure is demonstrated in Fig. 14 (for $\phi = 1$). The reduced models show a good agreement at higher pressure, with the error for RCPK42 goes from 10% at $P=1$ atm to 8% at $P=40$ atm, while for RCPK17 the error reduces from 14% to 9%. This is encouraging, given that application to high pressure is required for jet engines.

Figure 9: Comparison of species' profiles with RCPK17 (blue dashed lines), RCPK42 (blue solid lines) and detailed mechanism (red circles) for a laminar premixed flame at $\phi = 0.7$, $p=1$ atm and $T_u = 473$ K.
Figure 10: Comparison of species’ profiles with RCPK17 (blue dashed lines), RCPK42 (blue solid lines) and detailed mechanism (red circles) for a laminar premixed flame at $\phi = 1.0$, $p=1$ atm and $T_u = 403$ K.
Figure 11: Comparison of species’ profiles with RCPK17 (blue dashed lines), RCPK42 (blue solid lines) and detailed mechanism (red circles) for a laminar premixed flame at $\phi = 1.3$, $p=1$ atm and $T_u = 403$ K.
Figure 12: Comparison of species' profiles with RCPK17 (blue dashed lines), RCPK42 (blue solid lines) and detailed mechanism (red circles) for a laminar premixed flame at $\phi = 1$, $p=12$ atm and $T_u = 403$ K.
Figure 13: Laminar flame speeds with RCPK17 (blue dashed lines), RCPK42 (blue solid lines) and detailed mechanism (red circles) for varying equivalence ratio, at p=1 atm and $T_u = 403$ K.

Figure 14: Laminar flame speeds with RCPK17 (blue dashed lines), RCPK42 (blue solid lines) and detailed mechanism (red circles) for increasing pressure, at $\phi=1$ and $T_u = 403$ K.
4.3 Dynamic problems

In this section, the dynamic response of the RCCE-reduced mechanisms compared to the detailed mechanism is studied via two variations of the flamelet problem. In the first problem, an artificial pilot is applied close to stoichiometric mixture fractions to a flamelet initialised at unburnt composition, while a variation of this problem, where the flamelets are ignited with hot air (similar to [62]) is also investigated. In the second problem, a periodically-varying strain rate is imposed on a flamelet to test the dynamic response of the reduced mechanisms.

4.3.1 Igniting flamelet

The igniting flamelet has been employed in previous works by the authors, for generating data for training artificial neural networks [63] and for testing RCCE mechanisms [44]. We employ an unsteady flamelet where only a small part of the composition space - an artificial 'pilot' -, around the stoichiometric mixture fraction, is initialised with a burnt composition, the rest starting from unburnt composition. Therefore the unburnt mixture is gradually ignited, and the evolution of the temperature is visualised in Fig. 15, where a sharp temperature gradient is obtained for the ignition and then the mixture reaches equilibrium state.

The first case under examination is a flamelet at low strain rate $s = 300 \text{ s}^{-1}$, atmospheric pressure and temperature of fuel and oxidiser $T_u = 400 \text{ K}$. These conditions resemble the conditions at the previous comparisons in Sec. 4.1, while the pilot is applied between mixture fractions $z_1 = 0.06$ and $z_2 = 0.10$ for 300 steps and then removed; the timestep for these calculations is $10^{-7}\text{s}$ which means that the pilot was activated for 0.03ms. The results for this flamelet are shown in Fig. 16 for the evolution of temperature, two major products CO and CO$_2$ and a radical, H. There is only a small underprediction in RCPK17 for the values CO (less than 10%) and an overall underprediction for H. For both of these species the underprediction starts early enough, after 200 steps and remains until the steady-state. RCPK42 reproduces well all the transient profiles.
The second case in Fig. 17 is for a higher strain rate $s = 500 \, s^{-1}$, which is close to the extinction limit of RCPK17, and higher temperature $T_u = 600 \, K$ but same pressure. Similar response is obtained for both RCCE reduced mechanisms, apart from a small discrepancy in CO and H for RCPK17, which appears after the removal of the pilot. Overall, the igniting flamelet demonstrates the ability of the reduced mechanism to respond to transient conditions, and in particular such that could be encountered in igniting situations and also in piloted turbulent flames.

A different problem, which provides a more rigorous test for the ignition behaviour of the mechanisms, is the autoignition of a non-premixed flamelet from an unburnt condition by contact with hot air, studied by other authors as well [62]. In the case examined here, fuel is at $T_{u,\text{fuel}} = 400 \, K$, while air at $T_{u,\text{air}} = 2000 \, K$ at atmospheric pressure. The results are shown in Fig. 18, where the evolution of the laminar flamelet is shown from left to right after 100, 200 and 900 steps for temperature, CO, CO$_2$ and H$_2$ mass fractions. After 100 steps, the smaller RCPK17 underpredicts the ignition time and underpredicts by 300 K, while RCPK42 underpredicts by 150 K. The error in CO and CO$_2$ is similar, while H$_2$ is well reproduced.
After 900 steps (0.09ms) both mechanisms produce good predictions (the highest error being less than 10%) for all of the plotted species profiles and temperature. The same problem is also examined at a higher strain rate (Fig. 19), in order to further challenge the autoignition behaviour of the mechanisms. Both of the reduced models perform similarly to the lower strain rate case.
Figure 16: Transient profiles of CO, \(H\), \(\text{CO}_2\) mass fractions and temperature with RCPK17 (blue dashed lines), RCPK42 (blue solid lines) and detailed mechanism (red circles) for a laminar pilot-ignited flamelet at strain rate \(s = 300 \text{ s}^{-1}\), \(p=1\ \text{atm}\) and \(T_u = 400\ \text{K}\).
Figure 17: Transient profiles of CO, H, CO$_2$ mass fractions and temperature with RCPK17 (blue dashed lines), RCPK42 (blue solid lines) and detailed mechanism (red circles) for a laminar pilot-ignited flamelet at strain rate $s = 500$ s$^{-1}$, $p=1$ atm and $T_u = 600$ K.
Figure 18: Transient profiles of temperature, CO, CO₂ and H₂ mass fractions with RCPK17 (blue dashed lines), RCPK42 (blue solid lines) and detailed mechanism (red circles) for a laminar flamelet ignited by hot air at strain rate $s = 300 \text{ s}^{-1}$, $p=1 \text{ atm}$ and $T_{u,fuel} = 400 \text{ K} \ T_{u,air} = 2000 \text{ K}$.
Figure 19: Transient profiles of temperature, CO, CO$_2$ and H$_2$ mass fractions with RCPK17 (blue dashed lines), RCPK42 (blue solid lines) and detailed mechanism (red circles) for a laminar flamelet ignited by hot air at strain rate $s = 600$ s$^{-1}$, $p=1$ atm and $T_{u,fuel} = 400$ K $T_{u,air} = 2000$ K.
4.3.2 Non-premixed flamelet with time-dependent strain rate

The effect of a periodically varying strain rate on a laminar non-premixed flamelet is studied in three different cases: a) strain rate changing at 10 kHz, $p=1$ atm and unburnt temperature $T_u = 400$ K, b) strain rate changing at 20 kHz, $p=1$ atm and unburnt temperature $T_u = 400$ K and c) a case that approaches more realistic conditions for a jet engine with strain rate changing at 20 kHz, $p=12$ atm and unburnt temperature $T_u = 600$ K. To the authors’ knowledge, these conditions with the periodic strain rate have not been studied for a kerosene surrogate fuel.

A sinusoidal temporal variation is imposed on the strain rate, ranging from very low strain rates $s = 50$ s$^{-1}$ to high strain rates $s = 550$ s$^{-1}$, which is the extinction limit for the smaller mechanism RCPK17. The response obtained indicates that the two mechanisms are able to reproduce the dynamics of the detailed mechanism, as seen in Figs. 20, 21 and 22. The peak concentration of the major products CO, CO$_2$ and temperature at each time step are shown and it can be seen that they are accurately predicted from both mechanisms. In the case of smooth changes (10 KHz) in strain rate Fig. 20, the temperature is predicted well, but with a small deviation of around 70 K appears for the low strain rates (shown with dotted line). For the same case, the products CO, CO$_2$ are reproduced from both reduced mechanisms, showing a small error (around 10%) for CO after few periods and an overall underprediction of the peaks of CO$_2$ values for low strain rates. The results for acetylene are not as good as for the previous species, and an overall overprediction of this species is observed with RCPK17, while RCPK42 performs better and is able to follow the detailed mechanism after the third period with a decaying error. Regarding the case with more rapid changes (20 KHz) in strain rate Fig. 21, the response of the RCCE-reduced mechanisms is very similar to the previous one showing a better performance in temperature and species peak values, except of the C$_2$H$_2$ profiles.

In the last case we have attempted to test the mechanism at higher pressure and temperature, as could be encountered in a jet engine. The fuel and air in the unburnt streams are at 600 K and the pressure is 12 bar, while strain rate varies again at 20 KHz. The results shown in Figs. 20, 21 and 22 indicate that the two mechanisms RCPK17 and RCPK42 are able to reproduce the dynamics of
the full mechanism. At high strain rates, both reduced models underpredict the
temperature valleys by 20 K; furthermore, both mechanisms exhibit a deviation
in the prediction of acetylene, which is, however, alleviated after a while.
Figure 20: Temperature and profiles of peak mass fractions of CO₂, CO and C₂H₂ with RCPK17 (dashed lines), RCPK42 (solid lines) and detailed mechanism (dotted red) for a laminar non-premixed flamelet with time-dependent strain rate varying at 10 kHz, p=1 atm and $T_u = 400$ K.
Figure 21: Temperature and profiles of peak mass fractions of CO$_2$, CO and C$_2$H$_2$ with RCPK17 (dashed lines), RCPK42 (solid lines) and detailed mechanism (dotted red) for a laminar non-premixed flamelet with time-dependent strain rate varying at 20 kHz, p=1 atm and $T_u = 400$ K.
Figure 22: Temperature and profiles of peak mass fractions of CO$_2$, CO and C$_2$H$_2$ with RCPK17 (dashed lines), RCPK42 (solid lines) and detailed mechanism (dotted red) for a laminar non-premixed flamelet with time-dependent strain rate varying at 20 kHz, p=12 atm and $T_u$ = 600 K.

5 Conclusions

A methodology for deriving RCCE-reduced mechanisms via CSP was employed here for the development of two reduced chemical mechanisms for a surrogate fuel for kerosene. This is the first time that our RCCE-CSP methodology is used for such a complex and detailed mechanism of this scale, combined with surrogate fuels. This work not only tests the limits of our RCCE-CSP methodology, but those of RCCE as well. In addition to testing these limits, this is the first time that the igniting flamelet, the flamelet with different temperature between fuel and air and the unsteady flamelet with time-dependent strain rate are studied.

The CSP analysis employs a modified CSP pointer and laminar non-premixed flamelets calculated with the detailed mechanism and covering the whole range of
flammable strain rates. At first stage, several reduced mechanisms were created and compared in terms of their ability to reproduce the main characteristics of the detailed model in the non-premixed combustion regime including the extinction limits, temperature profiles, and major species profiles such as CO, CO$_2$ and C$_2$H$_2$. Two reduced mechanisms with 17 (RCPK17) and 42 (RCPK42) kinetically controlled species were chosen, the first one for compact size and low computational cost and the second one for accuracy. These two mechanisms were then tested and validated in the non-premixed regime for different strain rates, in laminar premixed flames for several mixture fractions, and then in several dynamic problems: a flamelet with an artificial pilot, a flamelet autoigniting by contact with hot air and a flamelet with time-dependent strain rate.

RCPK17 is a compact reduced mechanism with good performance in all combustion regimes in which it was tested, albeit not always quantitative. Better agreement is obtained for the flamelet problems, both steady-state and dynamic, where the agreement is often quantitative. It must be born in mind, however, that this mechanism extinguishes at lower strain rate than the detailed one. In terms of CPU time, RCPK17 is 17-19 times faster (depending on the problem) than the detailed mechanism and could thus be used for design purposes where repetitive calculations are required.

RCPK42 was found to reproduce quite accurately the detailed mechanism. This reduced mechanism performed well in the non-premixed regime, predicting all major species, the fuel components, intermediate hydrocarbons and extinction limits. In the premixed flames, good comparison was again obtained at lean, stoichiometric and rich conditions, at both atmospheric and high pressure conditions, though not quite as good as in the flamelet. The dynamic response of RCPK42 was also similar to the detailed mechanism, apart for a few cases such as the acetylene at the initial stages of the flamelet with time-dependent strain rate. RCPK42 achieved a significant speed-up of 6-8 times (depending on the problem) compared to the detailed model, and is therefore a robust and reasonably compact reduced mechanism for this kerosene surrogate.

The objective of developing reduced mechanisms for complex fuels is ultimately their incorporation into comprehensive simulations of turbulent combustion, such as those employing PDF methods. In such approaches, the vast majority of CPU
time is usually spent on integrating the reaction source term. The reduced mechanisms developed here aid not only in reducing this time by an order of magnitude, but also for providing lower-dimensional models suitable for tabulation via methods such as Artificial Neural Networks (ANNs). The RCCE-reduced mechanisms presented here, can form the basis for future reduced models optimised for CFD applications with the suggested surrogate fuel.

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References


