

RCCE-reduced chemical mechanisms for surrogate aviation fuels

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Abstract

Detailed mechanisms for aviation fuels contain hundreds of species and thousands of reactions, indicating a necessity for reduced mechanisms. Rate-Controlled Constrained Equilibrium (RCCE) provides a physical and mathematical framework for deriving reduced mechanisms, where the kinetically controlled (slow) species are determined from the kinetics of the detailed mechanism, while the equilibrated (fast or steady-state) species are calculated by minimising the Gibbs free energy of the system. In this work, reduced chemical mechanisms for the oxidation of kerosene are derived with RCCE. Several sets of constrained species for different surrogate fuels, based on n-decane or n-dodecane, lead to different reduced mechanisms and a considerable degree of reduction is obtained.

Introduction

CFD simulations of real problems, which require complex geometries, with comprehensive chemical mechanisms are computationally infeasible. Detailed mechanisms for aviation fuels may contain from few to hundreds of species and thousands of reactions, indicating a necessity for reduced mechanisms. Conventional methods for mechanism reduction are based on the approximation of quasi-steady-state (QSSA), with which differential equations are replaced with algebraic ones for species which are assumed to be in steady-state. However, the size of the complex mechanisms for surrogate aviation fuels may require considerable work in order to derive the reduced system of differential-algebraic equations.

RCCE provides a physical and mathematical framework for deriving reduced mechanisms, where the kinetically controlled species (which refer to non steady-state species for QSSA or slow species and are called constrained species) are determined from the kinetics of the detailed mechanism, without any assumption. The remaining species, which are called equilibrated (steady-state for QSSA or fast species) are calculated by minimising the Gibbs free energy of the system. This minimisation is subject to the constraint that the kinetically controlled species must maintain their concentrations as derived from chemical kinetics and also subject to the additional constraints of conserving energy, mass and elements. RCCE provides a general system of equations which are already parametrised in terms of the constrained species and does not require any individual derivation for different chemical mechanisms but only the identification of the constrained species. In this light, RCCE can easily provide the theoretical description for the reduction of different detailed chemical mechanisms for aviation fuels.

The common aviation fuel for aircrafts is kerosene, for both transport and military operations. Several surrogate fuels for kerosene have been proposed so far in order to match the physical and chemical properties of the real fuel and some of them include single component

fuels, like n-decane [1], while most of the later suggested ones consist of multiple components. These components are mainly n-paraffins, cyclo-paraffins and aromatics. N-paraffins are major components of these surrogate fuels, and particularly n-decane or n-dodecane are usually applied. Surrogates based on n-decane have been proposed by Honnet et al. [2], as the Aachen surrogate fuel, and by Gueret et al. [3], while surrogates based on n-dodecane are those of Violi et al. [4] and Cooke et al. [5]. Most of these surrogate fuels are accompanied by a chemical kinetics mechanism.

Chemical mechanisms are necessary to describe the oxidation of the hydrocarbons. Luche [6] introduced a reduced mechanism which consists of 89 species and 680 reactions to describe the oxidation of kerosene in a perfectly stirred reactor, which is the only skeletal mechanism for kerosene to our awareness. Luche et al. [7] used fuels based on n-decane, which seems to be the best candidate for a single component surrogate fuel, as in [3]. Dagaut et al. [8] developed another mechanism with 209 species and 1673 reactions to describe the oxidation of both kerosene and n-decane in a jet stirred reactor. They verified their results by conducting experiments using different types of surrogate fuels and kerosene and concluded to a 3-component fuel consisting of n-decane, n-propylbenzene and n-propylcyclohexane which describes the properties of kerosene best. Regarding mechanisms based on n-dodecane, Narayanaswamy et al. [9] developed a mechanism to describe the high temperature oxidation of n-dodecane and verified it against experimental results. They also used different kind of cyclo-paraffins, such as methylcyclohexane, and different aromatics, like m-xylene. Their mechanism consists of 367 species and 1892 reactions. The only reduced mechanism for kerosene oxidation is by Franzelli et al. [10], who introduced a two-step chemistry mechanism with 5 species and the fuel $C_{9.7396}H_{20.0542}$. Another ongoing effort is JetSurF 2.0 [11] in order to develop a Jet Surrogate Fuel mechanism. Further details on jet surrogates may be found in [12] or [13] while experiments on laminar burning velocity of commercial kerosene have been conducted by Vukadinovic et al. [14] and Kumar et al. [15] for a wide range of pressures and temperatures.

In this work, we present several reduced chemical me-

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chanisms derived via RCCE for the oxidation of kerosene using different sets of constrained species, different surrogate fuels and detailed mechanisms for kerosene and we obtain a considerable degree of reduction while maintaining the accuracy of species profiles.

RCCE formulation

RCCE is a method to describe chemical kinetics with a differential algebraic-system of equations (DAE). This system comprises a set of differential equations for the evolution of the constrained species, a set which is derived from the detailed mechanism, while a set of algebraic equations for the concentration of the fast species in constrained equilibrium is also included in the DAE system. The differential equation for the change in concentration of a constrained species c_i is given through the detailed mechanism

$$\frac{dc_i}{dt} = \sum_{j=1}^N \left[a_{ij}^c \sum_{k=1}^{NR} (v_{jk} r_k) \right] \quad (1)$$

where N is the total number of species, a_{ij}^c is a matrix which contains the contribution of each constrained species i to each species j , NR is the number of reactions, v_{jk} is the stoichiometric coefficient of the species j in reaction k and r_k is the reaction rate for reaction k . The concentration of a fast species j , c_j^* , is then calculated in constrained equilibrium by

$$c_j^* = \frac{P}{\rho RT} \exp\left(\frac{-\mu_j^o}{RT}\right) \exp\left[\sum_{i=1}^{M_e} \left(a_{ij}^e \lambda_i^e\right)\right] \exp\left[\sum_{i=1}^{M_c} \left(a_{ij}^c \lambda_i^c\right)\right], \quad (j = 1, \dots, N) \quad (2)$$

where μ_j^o is the chemical potential of species j in standard state, M_e is the number of elements, a_{ij}^e is a matrix which contains the contribution of each element i to each species j , λ_i^e are Lagrange multipliers of species i , M_c is the number of constrained species and λ_i^c are Lagrange multipliers for constrained species. The final form of the DAE system of RCCE is obtained by Eq. (1) and (2). The reader is referred to [16], [17] and [18] for further details on the RCCE derivation and application of RCCE to different problems and fuels.

Selection of constrained species

The only input parameter for RCCE is the identification of the kinetically controlled species, which has been based either on an empirical and trial-and-error basis or on methods for ordering the species' importance, such as Level of Importance (LOI) in [19] and [20]. LOI is a timescale analysis which identifies the species which are locally important by ordering the LOI indices for all species at a given condition (e.g. steady-state). The LOI index is a combination of the chemical lifetime of species and a sensitivity factor towards a given species, so that the LOI of species i at position x is given by

$$LOI_{i,x} = \tau_{i,x} S_{ij,x} \quad (3)$$

where the chemical lifetime $\tau_{i,x}$ of species i is an approximation calculated using the diagonal elements J_{ii} of the Jacobian matrix of the species and it is given by

$$\tau_{i,x} = -\frac{1}{J_{ii}} = -\frac{1}{\frac{\partial \omega_i}{\partial c_i}} = \frac{c_i}{\sum_{k=1}^{NR} (v'_{ik} - v''_{ik}) v'_{ik} r_k} \quad (4)$$

where v'_{jk} is the stoichiometric coefficient for reactants, v''_{jk} for products and r_k is given by

$$r_k = k_k \prod_{i=1}^N c_i^{v'_{ik}} \quad (5)$$

where k_k is the reaction rate coefficient. The sensitivity factor $S_{ij,x}$ is given by

$$S_{ij} = \left| \frac{\partial c_i}{\partial c_j} \right| = \left| \sum_{k=1}^{NR} \frac{dc_i}{dr_k} \frac{dr_k}{dc_j} \right| = \left| \sum_{k=1}^{NR} \left[\left(\sum_{l=1}^{NR} v_{lk} \right) \frac{v'_{lk} r_k}{c_j} \right] \right|. \quad (6)$$

Further details on LOI can be found in [21].

The determination of the species which must be constrained for the reduced mechanism results from an analysis on a steady-state solution. LOI is used for the purposes of this work in order to identify the constrained species for RCCE. In addition to LOI, species are ordered according to a criterion similar to LOI but using only the concentration of the species and the sensitivity factor. This Concentration and Sensitivity of species Criterion (CSC) is compared to LOI to identify the constrained species for RCCE. The CSC of species i at position x is given by

$$CSC_{i,x} = c_{j,x} S_{ij,x} \quad (7)$$

where $c_{j,x}$ is the concentration of species j at position x . Both CSC and LOI order the species locally, for different mixture fractions. An integration of these local criteria is applied, in order to identify the important species, over the mixture fraction space and weighted according to

$$LOI_i = \int_0^1 LOI_{i,x} dz = \sum_{x=z_1}^{z_2-1} LOI_{i,x} (z_{x+1} - z_x) \quad (8)$$

where z_x is the mixture fraction in position x , z_1 is the lowest mixture fraction and z_2 is the highest mixture. The integrated LOI and CSC for each species are ordered to identify the species which are globally important. These methods are also compared with a simpler one, which orders the species according to the concentration of species in steady-state only. Specifically, the highest concentration of each species all over the mixture fractions space is identified and then ordered, offering a fast criterion for the selection of the constrained species for RCCE. These methods are applied to the skeletal mechanism suggested by Luche [6] and to the detailed mechanism suggested by Narayanaswamy et al. [9] and are summarized in the

following Table 1. The surrogate fuels for both mechanisms are those which are suggested by the authors of the mechanisms and are shown in Table 2.

Three reduced mechanisms are derived for the Luche skeletal mechanism constraining species indicated from LOI, CSC and the maximum concentration method to demonstrate the applicability and efficiency of these methods. A detailed investigation of the methods for the selection of the constrained species for RCCE will follow in a future work. The reduced mechanisms are tested in a counterflow configuration (flamelet model [22]) and the profiles of major species, both constrained and unconstrained, are compared with those of the detailed mechanism. The strain rate for the following results is $s = 400s^{-1}$, with a timestep $t = 10^{-6}s$, for an 100 different mixture fractions.

Name	Species	Reactions
Luche skeletal [6]	89	680
Pitsch [9]	367	1825

Table 1: Chemical mechanisms for kerosene

Name	Components Names	Vol.	Formula
Kero A [3]	n-Decane	74%	$n-C_{10}H_{22}$
	n-Propylbenzene	15%	C_9H_{12}
	n-Cyclohexane	11%	C_9H_{18}
Kero B [9]	n-Methylcyclohexane	48.5%	C_7H_{17}
	n-Dodecane	30.3%	$n-C_{12}H_{26}$
	m-xylene	21.2%	C_8H_{10}

Table 2: Surrogate fuels for kerosene

Reduced mechanisms

Four reduced mechanisms are introduced for kerosene with RCCE, three of which are derived from the Luche skeletal mechanism and another reduced mechanism for the Pitsch mechanism. The constrained species for these mechanisms are identified with LOI, CSC and using the species with the highest concentrations. In particular, the reduced sets for Luche mechanism are derived with LOI, CSC and the criterion for maximum concentration while the Pitsch mechanism is reduced constraining species with the maximum concentration. The three sets of constrained species for the Luche mechanism are shown in Table 3.

The number of the species which are retained in the reduced mechanism is set to 25, as this number was enough to contain some very major species and the fuel compo-

	Max Conc	CSC _{CO}	LOI _{C₂H₂}
1	N_2	H_2O	$n-C_{10}H_{22}$
2	$n-C_{10}H_{22}$	O_2	O_2
3	O_2	O	CO
4	C_9H_{12}	H	H_2O
5	H_2O	H_2	H_2
6	C_9H_{18}	CO	C_9H_{12}
7	CO	C_2H_4	C_2H_4
8	CO_2	OH	CH_4
9	H_2	CO_2	CO_2
10	C_2H_4	CH_4	C_9H_{18}
11	CH_4	$n-C_{10}H_{22}$	O
12	C_2H_2	CH_3	H
13	C_3H_6	C_2H_2	C_2H_2
14	H	C_7H_7	C_6H_6
15	OH	C_9H_{18}	C_3H_6
16	O	C_9H_{12}	C_7H_8
17	C_6H_6	C_3H_6	$a-C_3H_4$
18	C_2H_6	CH_2	$p-C_3H_4$
19	C_7H_8	C_3H_5	OH
20	C_3H_5	$p-C_3H_4$	C_3H_5
21	$a-C_3H_4$	$a-C_3H_4$	C_2H_6
22	$p-C_3H_4$	C_9H_{17}	CH_3
23	C_4H_6	C_3H_3	C_4H_6
24	CH_3	CH_2O	C_7H_7
25	C_3H_2	C_6H_6	C_4H_4

Table 3: Sets of constrained species for the Luche mechanism

nents, for all sets. C_2H_2 was selected as target for LOI and CO was selected as target for CSC.

The three reduced mechanisms for the Luche mechanism are compared with those of the detailed mechanism in Fig.1 - 8. The results for the reduced mechanism constraining species from the LOI order are shown with circles, the reduced mechanism with CSC species with triangles, the reduced mechanism with the species with highest concentration are shown with squares and the detailed mechanism with red solid line. It is obvious that the three reduced mechanisms have similar accuracy, as it was expected by looking at the sets of constrained species in Table 3. Most profiles of major species like O_2 , CO , H_2 and the fuel components are reproduced as it is shown in Fig1 - 8. The reduced mechanism constraining the species with the highest concentration provides the highest accuracy and the species profiles are very well predicted.

One more reduced mechanism is derived for the Pitsch detailed mechanism using the maximum concentration method, as this method provided the highest accuracy for the reduction of Luche mechanism. The 35 species with maximum concentration are constrained, as this set was found to include the major species and to provide good accuracy in the species profiles for this problem.

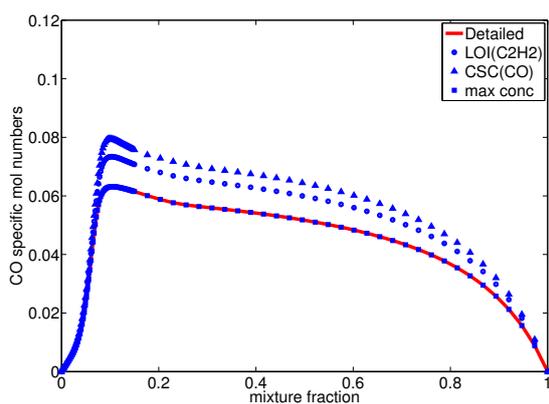


Figure 1: CO using the Luche detailed mechanism (solid line), RCCE with 25 species from $LOI_{C_2H_2}$ (circles), from CSC_{CO} (triangles) from maximum concentration (squares)

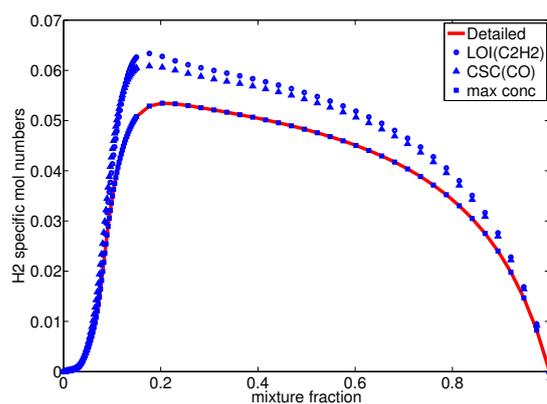


Figure 4: H_2 using the Luche detailed mechanism (solid line), RCCE with 25 species from $LOI_{C_2H_2}$ (circles), from CSC_{CO} (triangles) from maximum concentration (squares)

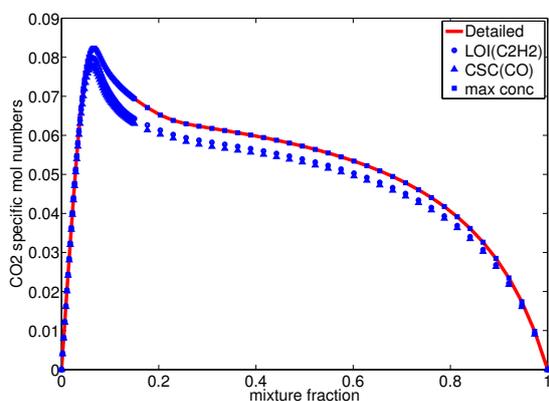


Figure 2: CO_2 using the Luche detailed mechanism (solid line), RCCE with 25 species from $LOI_{C_2H_2}$ (circles), from CSC_{CO} (triangles) from maximum concentration (squares)

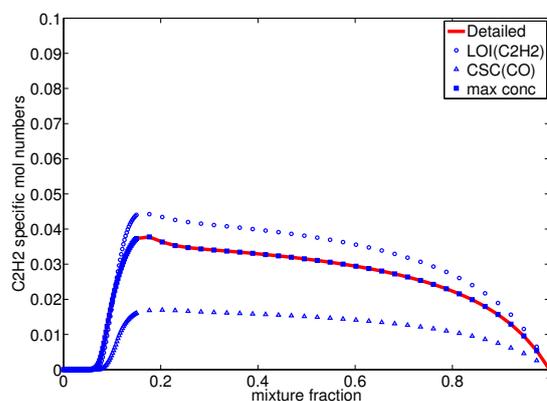


Figure 5: C_2H_2 using the Luche detailed mechanism (solid line), RCCE with 25 species from $LOI_{C_2H_2}$ (circles), from CSC_{CO} (triangles) from maximum concentration (squares)

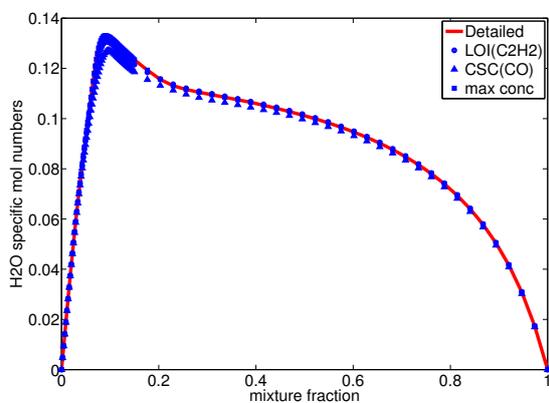


Figure 3: H_2O using the Luche detailed mechanism (solid line), RCCE with 25 species from $LOI_{C_2H_2}$ (circles), from CSC_{CO} (triangles) from maximum concentration (squares)

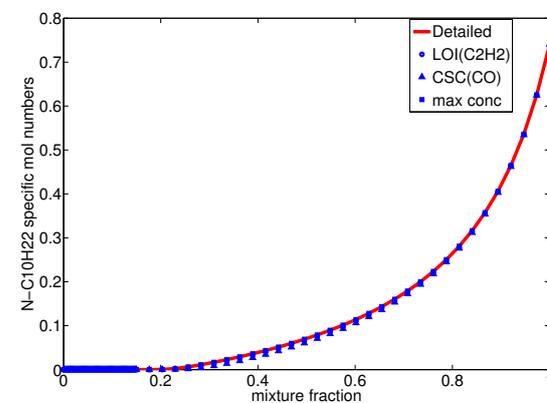


Figure 6: n-Decane using the Luche detailed mechanism (solid line), RCCE with 25 species from $LOI_{C_2H_2}$ (circles), from CSC_{CO} (triangles) from maximum concentration (squares)

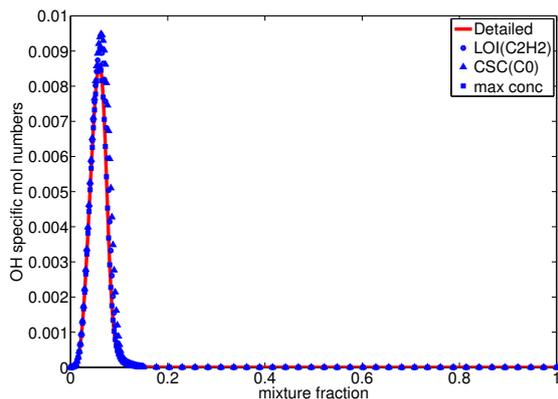


Figure 7: OH using the Luche detailed mechanism (solid line), RCCE with 25 species from $LOI_{C_2H_2}$ (circles), from CSC_{CO} (triangles) from maximum concentration (squares)

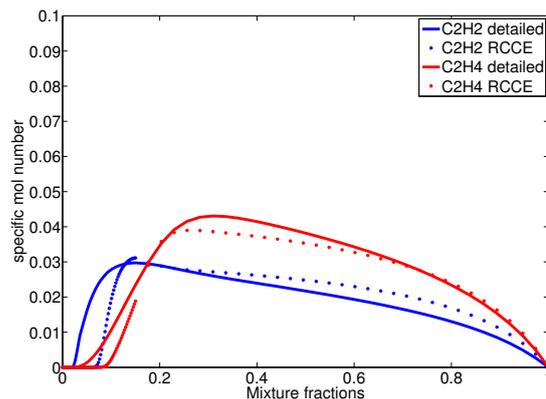


Figure 9: C_2H_4 and C_2H_2 for the Pitsch detailed mechanism (solid line) and RCCE with 35 species from maximum concentration (circles)

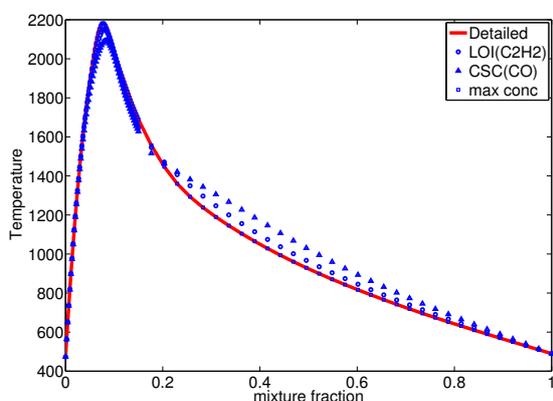


Figure 8: Temperature using the Luche detailed mechanism (solid line), RCCE with 25 species from $LOI_{C_2H_2}$ (circles), from CSC_{CO} (triangles) from maximum concentration (squares)

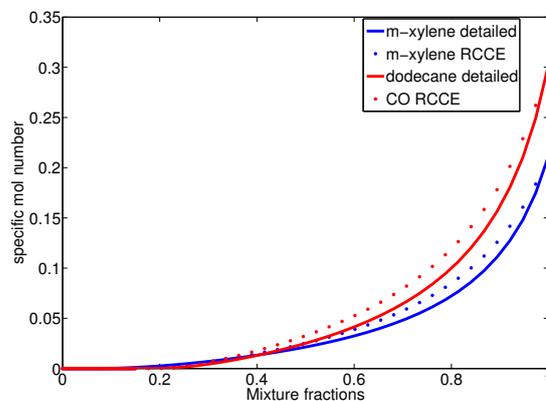


Figure 10: m-xylene and n-dodecane for the Pitsch detailed mechanism (solid line) and RCCE with 35 species from maximum concentration (circles)

These species are N_2 , C_7H_{14} , $n-C_{12}H_{26}$, C_8H_{10} , O_2 , H_2O , CH_4 , CO , H_2 , CO_2 , $C_6H_8O_2$, C_2H_4 , C_2H_2 , $C_{16}H_{10}$, OH , C_3H_6 , H , O , C_6H_6 , C_4H_6 , $p-C_3H_4$, C_2H_6 , C_7H_8 , $a-C_3H_4$, C_5H_6 , C_3H_3 , C_8H_6 , CH_3 , C_5H_{10} , C_4H_2 , CH_2CO , C_6H_{10} , $C_{10}H_8$, $i-C_5H_8$, $p-C_4H_8$. Important species for the reduced mechanisms, such as O , O_2 , CO , CO_2 , H , H_2 , OH and H_2O as well as important species for soot formation such as benzene (C_6H_6), acetylene (C_2H_2) and pyrene ($C_{16}H_{10}$) are identified.

Again major species such as C_2H_2 , C_2H_2 and two of the fuel components $n-C_{12}H_{26}$ and C_8H_{10} are very well predicted with RCCE. The profiles of the above mentioned species are predicted with high accuracy with RCCE providing a reduction in computational cost of 12 - 15 times.

Discussion

Several reduced sets for kerosene are derived in this work using three different methods for the identification of the constrained species for RCCE. These methods are

LOI, CSC and simply the species with the highest concentration. RCCE was able to predict the concentration of major species, like CO , C_2H_2 , H_2 and fuel components for the oxidation of kerosene in mixture fraction space. RCCE predicted the concentration of these major species even when constraining different sets of species indicating a flexibility of the method. Future work will include verification of the reduced sets for ignition delay time and burning velocity as well as further reduction in the number of the constrained species. An investigation of the optimal way for identifying the best number of constrained species is also among our future tasks.

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References

- [1] P. Dagaut, M. Reuillon, J.-C. Boettner, and M. Cathonnet. Int. Symp. on Combustion 25 (1) (1994), 919–926.
- [2] S. Honnet, K. Seshadri, U. Niemann, and N. Peters. Proceedings of the Combustion Institute 32 (2009), 485–492.
- [3] C. Gueret, M. Cathonnet, J.-C. Boettner, and F. Gaillard. Symposium (International) on Combustion 23 (1991), 211–216.
- [4] A. Violi, S. Yan, E. G. Eddings, A. F. Sarofim, S. Granata, T. Faravelli, and E. Ranzi. Combustion Science and Technology 174 (11-12) (2002), 399–417.
- [5] J. A. Cooke, M. Bellucci, M. D. Smooke, A. Gomez, A. Violi, T. Faravelli, and E. Ranzi. Proceedings of the Combustion Institute 30 (1) (2005), 439–446.
- [6] J. Luche. “Elaboration of reduced kinetic models of combustion. Application to a kerosene mechanism”. PhD thesis. LCSR Orleans, 2003.
- [7] J. Luche, M. Reuillon, J.-C. Boettner, and M. Cathonnet. Combustion Science and Technology 176 (11) (2004), 1935–1963.
- [8] P. Dagaut, A. El Bakali, and A. Ristori. Fuel 85 (78) (2006), 944–956.
- [9] K. Narayanaswamy, P. Pepiot, and H. Pitsch. Combustion and Flame 161 (4) (2014), 866–884.
- [10] B. Franzelli, E. Riber, M. Sanjos, and T. Poinso. Combustion and Flame 157 (7) (2010), 1364–1373.
- [11] H. Wang, E. Dames, B. Sirjean, D. A. Sheen, R. T. A. Violi, J. Y. W. Lai, F. N. Egolfopoulos, D. F. Davidson, R. K. Hanson, C. T. Bowman, C. K. Law, W. Tsang, N. P. Cernansky, D. L. Miller, and P. Lindstedt. *A high-temperature chemical kinetic model of n-alkane (up to n-dodecane), cyclohexane, and methyl-, ethyl-, n-propyl and n-butyl-cyclohexane oxidation at high temperatures*. 2010. URL: <http://melchior.usc.edu/JetSurF/JetSurF2.0>.
- [12] T. Edwards, M. Colket, N. Cernansky, F. Dryer, F. Egolfopoulos, D. Friend, E. Law, D. Lenhart, P. Lindstedt, H. Pitsch, A. Sarofim, K. Seshadri, M. Smooke, W. Tsang, and S. Williams. “Development of an Experimental Database and Kinetic Models for Surrogate Jet Fuels”. *Aerospace Sciences Meetings*. American Institute of Aeronautics and Astronautics, 2007.
- [13] P. Dagaut and M. Cathonnet. Progress in Energy and Combustion Science 32 (1) (2006), 48–92.
- [14] V. Vukadinovic, P. Habisreuther, and N. Zarzalis. Fuel 111 (0) (2013), 401–410.
- [15] K. Kumar, C.-J. Sung, and X. Hui. Fuel 90 (3) (2011), 1004–1011.
- [16] W. Jones and S. Rigopoulos. Proceedings of the Combustion Institute 30 (1) (2005), 1325–1331.
- [17] W. Jones and S. Rigopoulos. Combustion and Flame 142 (3) (2005), 223–234.
- [18] W. P. Jones and S. Rigopoulos. Combustion Theory and Modelling 11 (5) (2007), 755–780.
- [19] T. Lovas, S. Navarro-Martinez, and S. Rigopoulos. Proceedings of the Combustion Institute 33 (1) (2011), 1339–1346.
- [20] S. Rigopoulos and T. Lovas. Proceedings of the Combustion Institute 32 (1) (2009), 569–576.
- [21] T. Lovas. Combustion and Flame 156 (7) (2009), 1348–1358.
- [22] P. T. and V. D. *Theoretical and Numerical Combustion*. Edwards, 2001.