

Simplified Chemical Kinetic Models for High-Temperature Oxidation of C₁ to C₁₂ *n*-alkanes

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Abstract

In a recent study, we have shown that for high-temperature combustion of *n*-dodecane, the kinetics of fuel cracking to form smaller molecular fragments is fast and may be decoupled from the oxidation kinetics of the fragments. Consequently, the model could be considerably reduced while maintaining good agreement with a large range of experimental data. In this study we expand this approach, starting from JetSurF v.0.2, for all *n*-alkanes up to *n*-dodecane to consistently explore the role of fuel cracking in paraffin combustion. JetSurF (<http://melchior.usc.edu/JetSurF>) is a detailed chemical kinetic model for the combustion of jet-fuel surrogate that is being developed through a multi-university research collaboration. The current 0.2 version describes the pyrolysis and oxidation kinetics of normal alkanes up to *n*-dodecane at high temperatures. This model has been extensively validated against a large set of experimental data and for a wide range of conditions, for each *n*-alkane from methane to *n*-dodecane. In addition, a fully reduced model describing the combustion of *n*-alkanes from C₁ to C₁₂ is proposed emphasizing the key common reactions of the combustion of aliphatic hydrocarbons at high temperatures.

Introduction

Surrogate fuels are mixtures of pure hydrocarbon compounds developed to mimic the combustion behavior of real jet fuels. This approach was developed to simulate jet fuel combustion properties with detailed chemical kinetic models [1]. However, starting from a single molecule and adding other compounds to develop a fuel surrogate increases kinetic complexity considerably. Surrogate kinetics remains fundamentally difficult because of the underlying uncertainties and kinetic coupling among the products of fuel decomposition. In a recent study, we have shown that one possible way to address the problem of kinetic coupling of cracking products is to simplify the detailed kinetic model of the fuel component [2]. In this approach, fuel cracking is assumed to be fast relative to the oxidation of molecular fragments ranging from C₁ to C₄, and as such cracking of the parent fuel molecules may be treated by a lumped model. Indeed it was demonstrated in our earlier study [2] that for high-temperature combustion of *n*-dodecane—a typical surrogate component, fuel cracking to form smaller molecular fragments is fast and may be decoupled from the oxidation kinetics of these fragments. As the result, the model could be reduced considerably, while maintaining good agreement with a wide range of experimental data.

In this study, we expand this approach for all *n*-alkanes from *n*-pentane up to *n*-dodecane to explore the role of fuel cracking in paraffin combustion consistently. We propose a systematic, simple and consistent method to simplify detailed chemical kinetic models of *n*-alkanes. The simplification procedure is applied to JetSurF v.0.2

[3], a work-in-progress, detailed chemical model for the combustion of jet-fuel surrogate developed through a multi-university research collaboration. The simplified model is validated extensively against a large set of experimental data and over a wide range of conditions, for all *n*-alkane from methane to *n*-dodecane. In addition, a lumped model describing the combustion of *n*-alkanes from C₁ to C₁₂ is proposed emphasizing the key common reactions of the combustion of aliphatic hydrocarbons at high temperatures.

Detailed Kinetic Model

JetSurF v.0.2 [3] is briefly described in this section. The reaction model consists of 194 species and 1459 reactions (hereafter referred to as Model I). It describes the pyrolysis and oxidation kinetics of normal alkanes up to *n*-dodecane at high temperatures. The development effort centers on achieving consistent kinetic parameter assignment and predictions for a wide range of hydrocarbon compounds. The base model is USC-Mech II (111 species, 784 reactions) that describes the oxidation of H₂ and CO and the high-temperature chemistry of C₁-C₄ hydrocarbons [4].

The base model is augmented with a set of reactions (83 species and 675 reactions) to describe high-temperature pyrolysis and oxidation of normal alkanes (C_kH_{2k+2}, 5 ≤ k ≤ 12). More details on the kinetic parameters of the reaction classes used in the *n*-alkane model can be found on the JetSurF website. Additionally, JetSurF contains a lumped 4-species, 12-step *n*-dodecane oxidation model to partially capture the low- to intermediate-temperature chemistry. Although the use of

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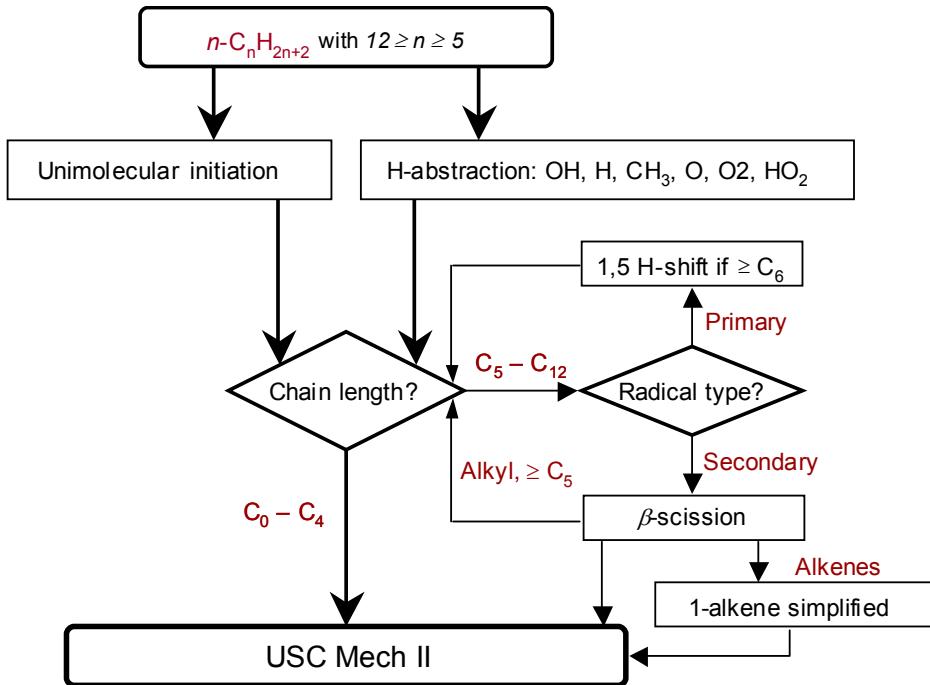


Figure 1. Systematic simplification of a detailed *n*-alkane reaction model.

this model does not offer the possibility to closely predict the low-temperature chemistry, it enables a better understanding of the impact of low- to intermediate-temperature chemistry on *n*-dodecane oxidation at high temperatures.

Simplified *n*-alkanes Model and Detailed USC-Mech II

We propose a systematic way to simplify the detailed *n*-alkane model. This approach continues the effort made in JetSurF to achieve consistent kinetic parameter assignment and predictions for a wide range of *n*-alkane compounds and is shown schematically in Figure 1.

From an initial $n\text{-C}_n\text{H}_{2n+2}$, initial C-C bond fission leads to two primary alkyl radicals $\text{C}_i\text{H}_{2i+1} + \text{C}_j\text{H}_{2j+1}$ with $i+j = n$. The chain length i and j are then tested:

1. If i and $j \leq 4$ then the alkyl radical oxidation reactions are described in the detailed kinetic model, USC-Mech II.
2. If i or $j > 4$, 1,5 H-shift is allowed if i or $j \geq 6$. This step leads to primary and secondary radicals, which undergo decomposition by β -scission leading to primary alkyl radicals and 1-alkenes $1\text{-C}_k\text{H}_{2k}$.
3. Primary radicals formed in step 2 are examined again in steps 1 and 2 until the products of their β -scission can be described by USC-Mech II. Depending on the size of 1-alkenes formed, their reactions of these species are described by USC-Mech II, if $k \leq 4$, or by a simplified 1-hexene / 1-pentene sub-mechanism if $5 \leq j \leq 6$.
4. Small radicals formed during the process react through H-abstraction by OH, H, CH₃, O, O₂, HO₂, leading to

primary and secondary radicals., whose further decomposition reactions are described in steps 1 to 3.

This procedure produces a lumped model composed of semi-global reactions whose rate parameters are taken from JetSurF v.0.2. Rate parameters of initial C-C bond fissions are chosen to be those of the C-C fission of each *n*-alkane of the detailed model, i.e., the reverse rates of $p\text{-C}_i\text{H}_{2i+1} + p\text{-C}_j\text{H}_{2j+1} = n\text{-C}_n\text{H}_{2n+2}$. For H-abstraction followed by β -scission, we used the rate coefficient of the H-abstraction reactions since the subsequent β -scission is usually fast and not rate limiting [2]. The skeletal sub-model for 1-hexene and 1-pentene contains 10 reactions and was derived initially from JetSurF v.0.2 using the method described in [5]. As shown in Table 1, reactions 4 and 9 are lumped, semi-global reactions, since the products of H-abstraction are expected to dissociate rapidly through β -scission.

The final lumped model for *n*-alkane cracking is composed of a total of 9 species, i.e., from *n*-pentane to *n*-dodecane less undecane plus 1-pentene and 1-hexene. This represents a considerable simplification over the detailed chemistry of *n*-alkanes in JetSurF v.0.2 (83 species and 675 reactions). Combined with USC-Mech II, the total simplified model features 120 species and 977 reactions describing the pyrolysis and oxidation kinetics of all normal alkanes up to *n*-dodecane at high temperatures. This model will be referred to as the Model II in the remaining text.

Table 1. Simplified 1-alkenes C_kH_{2k} model for $k = 5$ and 6^a

No.	Reaction	A	n	E_a
1	$C_6H_{12} \rightleftharpoons aC_3H_5 + nC_3H_7$	1.07×10^{23}	-2.03	74960
2	$C_6H_{12} + H \rightleftharpoons C_2H_4 + pC_4H_9$	8.00×10^{21}	-2.39	11180
3	$C_6H_{12} + H \rightleftharpoons C_3H_6 + nC_3H_7$	1.60×10^{22}	-2.39	11180
4	$C_6H_{12} + H \rightleftharpoons C_4H_6 + C_2H_5 + H_2$	5.40×10^4	2.50	-1900
5	$C_6H_{12} + O \rightleftharpoons C_2H_4 + nC_3H_7 + HCO$	3.30×10^8	1.45	-402
6	$C_5H_{10} \rightleftharpoons aC_3H_5 + C_2H_5$	7.24×10^{22}	-1.94	75470
7	$C_5H_{10} + H \rightleftharpoons C_2H_4 + nC_3H_7$	8.00×10^{21}	-2.39	11180
8	$C_5H_{10} + H \rightleftharpoons C_3H_6 + C_2H_5$	1.60×10^{22}	-2.39	11180
9	$C_5H_{10} + H \rightleftharpoons C_4H_6 + CH_3 + H_2$	5.40×10^4	2.50	-1900
10	$C_5H_{10} + O \rightleftharpoons pC_4H_9 + HCO$	3.30×10^8	1.45	-402

^a Rate coefficient expressed as $k = AT^n \exp(-E_a/RT)$. Units are mol, cm, sec, cal, and K.

Simplified *n*-alkanes Model and Skeletal USC-Mech II

A skeletal USC-Mech II was also developed specifically to capture the oxidation kinetics for the fragments of *n*-alkane cracking. Starting from USC-Mech II (111 species, 784 reactions), the detailed reaction model was reduced to a skeletal model using the method of [5]. The reduction is based on testing the reaction and reaction-enthalpy rates of the detailed reaction model. Here the generation of the skeletal model used a range of flame speed simulations using PREMIX [6]. Equivalence ratios ranged from 0.7 to 1.5, and four *n*-alkane flames were employed to yield the reaction rate and heat flux map: *n*-heptane ($p = 1$ atm and $T = 353.15$ K), *n*-nonane ($p = 1$ atm and $T = 403.15$ K), *n*-decane ($p = 1$ atm and $T = 403.15$ K) and *n*-dodecane ($P = 1$ atm and $T = 403.15$ K). The final skeletal model features 75 species and 306 reactions. This skeletal model was then combined with the lumped model of *n*-alkane cracking. In whole, the final model describing the oxidation and pyrolysis of all *n*-alkanes up to *n*-dodecane contains 84 species and 499 reactions. This model is henceforth referred to as Model III.

Computational approach

Table 2 summarizes the three models of different levels of simplicity that were used for computation.

Table 2. Summary of reaction models used in simulations
(The models are available at <http://melchior.usc.edu/JetSurF/>)

Model	n-Alkane cracking	H ₂ /CO/C ₁ -C ₄ based model	Number of species	Number of reactions
I	detailed ^a	detailed ^b	194	1459
II	lumped ^c	detailed ^b	120	977
III	lumped ^c	skeletal ^d	84	499

^a JetSurF 0.2. ^b USC Mech II. ^c JetSurF 0.2 reduced in size by lumping. ^d skeletal USC Mech II

Freely propagating and burner-stabilized flames were performed using the Sandia Premix code [6] using the mixture-averaged transport analysis and including thermal diffusion. Simulations were performed using multicomponent analysis on a limited number of fuels.

The results showed no significant discrepancies between this approach and mixture-averaged formula. The transport properties of *n*-alkanes and *n*-alkenes (C_nH_{2n+2} and C_nH_{2n} , $5 \leq n \leq 12$) were taken from [7]. The Lennard-Jones 12-6 potential parameters were estimated systematically using the approach similar to that of [8] and may be found at <http://melchior.usc.edu/JetSurF/>. Simulations of the ignition delay behind reflected shock waves assumed adiabatic and constant volume conditions with the ignition criteria made consistent with the experiments. Flow reactor simulations used constant temperature and pressure assumptions.

Results and discussion

Models II and III were validated against a large set of experimental data, including fuel pyrolysis in a jet-stirred reactor, laminar flame speeds, and ignition delay times behind reflected shock waves and for a wide range of conditions for each *n*-alkane from *n*-pentane to *n*-dodecane. Only selected validations are presented here; the full set of validation plots can be found at <http://melchior.usc.edu/JetSurF/>. The following standard of presentation is adopted through all figures: the dotted lines represent prediction of Model I (detailed JetSurF v 0.2); dashed lines represent results of Model II; solid lines represent the prediction by the simplest model – Model III.

Predictions of the detailed model were compared to experimental data available for *n*-dodecane pyrolysis. Figure 2 depicts the conversion of *n*-dodecane during its pyrolysis in a jet-stirred reactor as a function of temperature and residence time. Models II and III capture the conversion rate of *n*-dodecane closely.

Figure 3 depicts experimental and numerical results of ignition delay times of selected *n*-alkane-oxygen-nitrogen (or argon) mixtures behind reflected shock waves. Only results for *n*-octane, to *n*-dodecane at different equivalence ratios and pressures are presented here. A full set of validation plots for all *n*-alkanes can be found at <http://melchior.usc.edu/JetSurF/>. As seen, the agreement between the simplified and skeletal models is good compared to the full model (Model I) and

experimental data. No low-temperature sub model is included in Models II and III. Therefore, it is not surprising that these models overpredict the ignition delays towards low-temperature. In principle, the lumped low-temperature could be included in Models II and III but this is not attempted here since our goal is a lumped model for the high-temperature oxidation of *n*-alkanes.

Experimental and numerical laminar flame speeds of *n*-dodecane are shown in Fig. 4. Again, results for other *n*-alkanes can be found at the JetSurF web site. An excellent agreement is observed between simplified and skeletal models compare to the predictions of the full model and the experimental data.

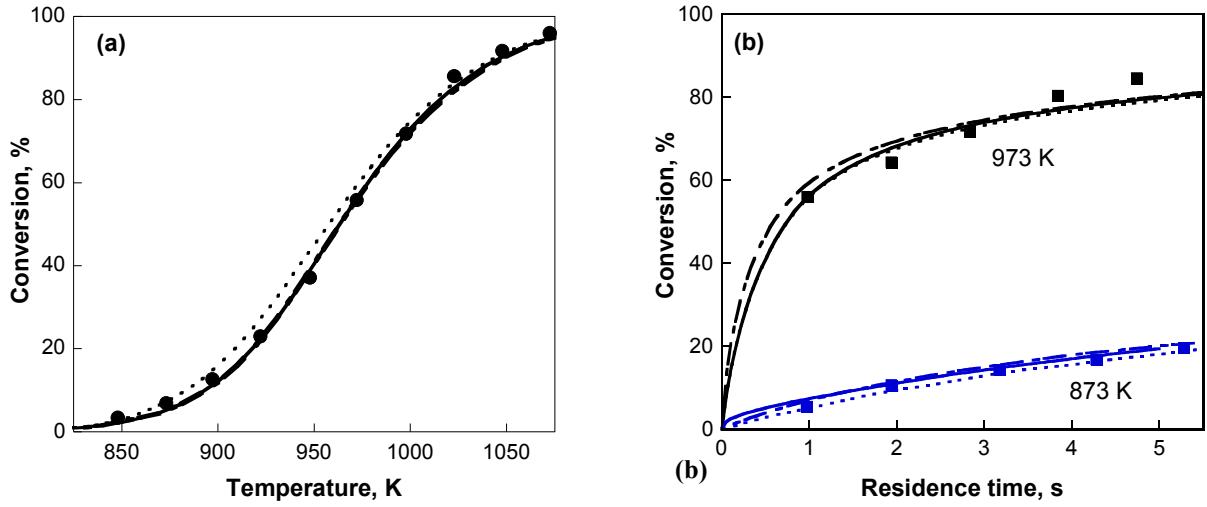


Figure 2. Experimentally (symbols [9]) and numerically determined conversion of *n*-C₁₂H₂₆ as a function of (a) temperature ($p = 1$ atm, residence time = 1 s) and (b) residence time ($p = 1$ atm) for the pyrolysis of 2% *n*-C₁₂H₂₆ in He, both in a jet stirred reactor. Dotted line: Model I, dash line: Model II, solid line: Model III.

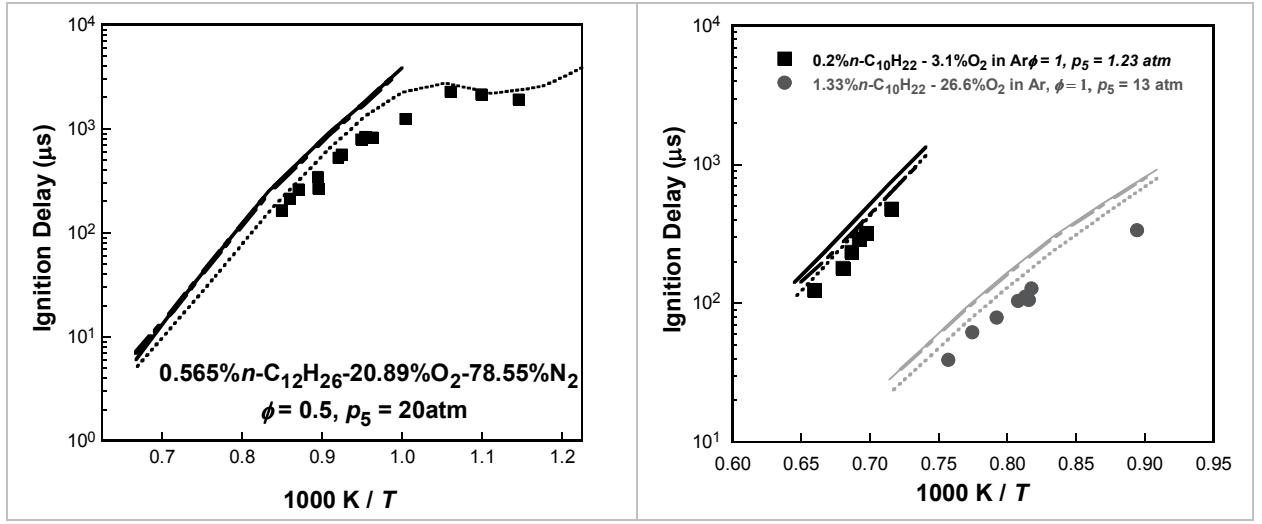


Figure 3. Experimentally (symbols all from Hanson and co-workers [10,11] except *n*-C₁₀H₂₂ at 13 atm from [12]) and numerically determined ignition delay times for *n*-dodecane and *n*-decane oxidation behind reflected shock waves. Dotted line: Model I, dash line: Model II, solid line: Model III.

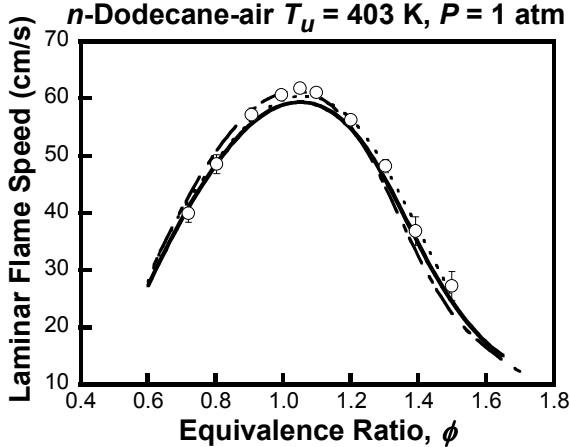


Figure 3: Experimentally [2] (symbols) and numerically determined laminar flame speeds of *n*-dodecane/air mixtures. Dotted line: Model I, dash line: Model II, solid line: Model III.

Validation tests against global combustion properties, including ignition delay times and laminar flame speeds, show that the lumped and skeletal models are accurate and capture the principal reaction kinetic feature of the detailed chemical kinetic model.

Perhaps an even more important test is to validity of the simplified model against detailed species profiles. Here we compare the predictions of Models II and III to data collected for *n*-dodecane pyrolysis in jet-stirred reactor. Figure 4 presents these results for 10 species, including C₂H₄, CH₄, C₃H₆, H₂, 1-C₄H₈, 1,3-C₄H₆, 1-C₅H₁₀, 1-C₆H₁₂, C₆H₆ (benzene) and aC₃H₄ (allene). It can be seen that Models II and III capture the principal features of product distribution correctly. Kinetic details lost in the lumping process, particularly the absence of exhaustive isomerization channels for the alkyl radicals, do lead to notable variations in the minor product distributions. It can be argued that uncertainties in experimental results can be important given possible problems like mass conservation, cocking, uncertainty in residence time and temperature, and possibility of wall-reactions. Hence we do not consider the discrepancies observed for the simplified models II and III from the detailed model I to be significant.

Hanson and co-workers [13,14] reported OH and CH₃ concentrations as a function of time for *n*-heptane oxidation behind reflected shock waves. Comparison between these experimental results and simulations are depicted in Figure 5.

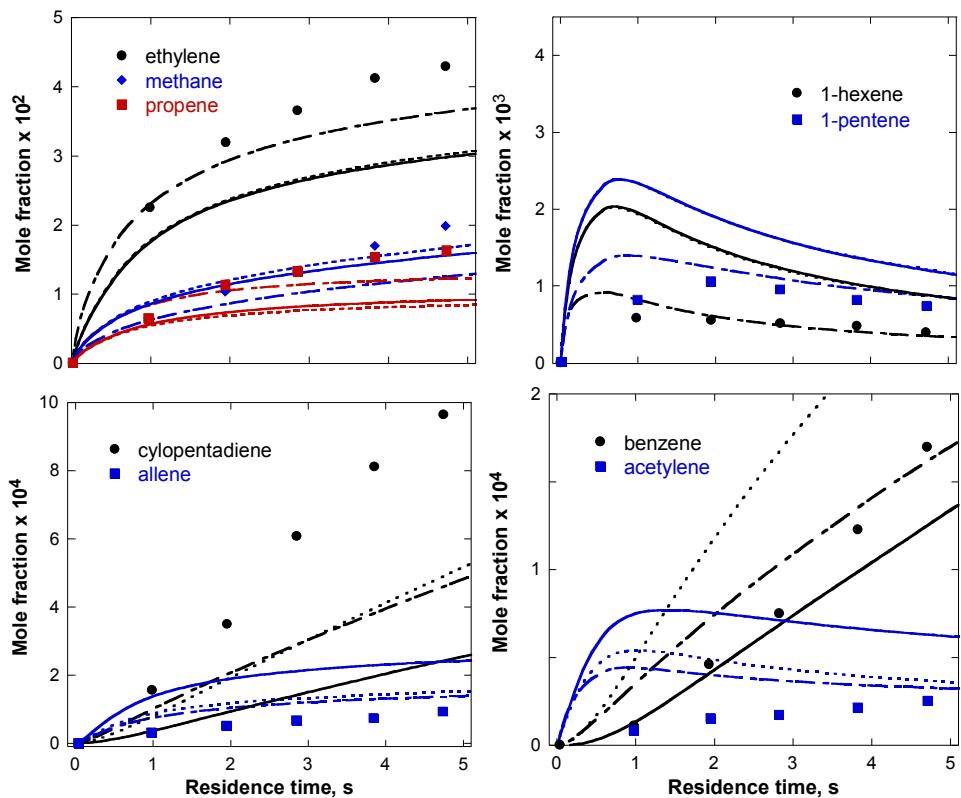


Figure 4: Experimentally [9] (symbols) and numerically determined species profiles from the pyrolysis of 2% *n*-C₁₂H₂₆ in He in a jet stirred reactor. Dotted line: Model I, dash line: Model II, solid line: Model III.

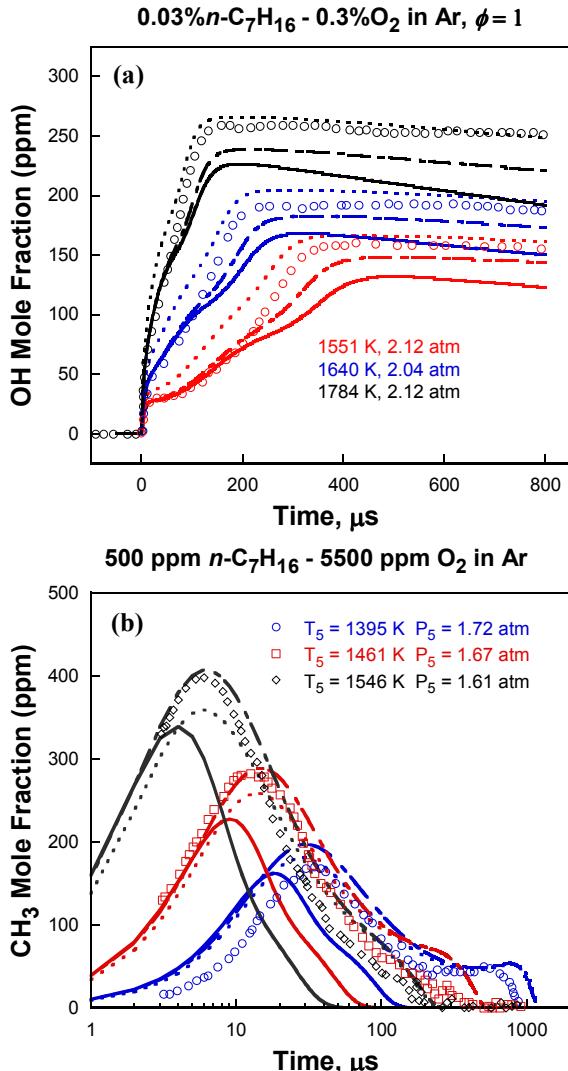


Figure 5: Experimentally (symbols) and numerically (solid line: skeletal model; dash line: simplified model; dotted line: JetSurF v. 0.2) determined OH [14] (a) and CH₃ [15] (b) mole fractions as a function of time for *n*-heptane oxidation behind reflected shock waves.

It is seen that Models II and III capture principal features of OH mole fractions correctly. The time histories for OH are particularly well described during early induction times. However, the simplified model underestimate the mole fraction OH in the plateau region. As seen in Figure 5, Models II and III also predict the radical CH₃ species profile rather well accurately. Interestingly, Model II is also able to predict the plateau observed experimentally towards the end of CH₃ disappearance. Maximum CH₃ mole fraction is under predicted, however, with Model III. Additionally, the plateau is lost. The time dependent CH₃ species profiles illustrate that, in the case of *n*-heptane, reducing the base model into a skeletal form from flame responses can disable its ability to capture fine features of

transient free radical concentrations. In principle, this feature can be recovered by including the reactions relevant for this particular chemistry.

Simulation results suggest that for a wide range of combustion conditions, the assumption that kinetics of fuel cracking to form smaller molecular fragments is fast and can be decoupled from the oxidation kinetics of the fragments is adequate. Global combustion parameters, including ignition delays and flame speeds can be well described using a simplified *n*-alkane model along with a detailed mechanism that describes the oxidation of H₂ and CO and the high-temperature chemistry of C₁-C₄ hydrocarbons. In addition, the use of a skeletal version of the H₂/CO/C₁-C₄ reaction model generally leads to satisfactory results.

Conclusion

In this work, we demonstrated that for high-temperature combustion of *n*-alkanes up to *n*-dodecane, the kinetics of fuel cracking to form smaller molecular fragments is fast and may be decoupled from the oxidation kinetics of the fragments. We propose a systematic and consistent method to generate a lumped *n*-alkane model starting from JetSurF v.0.2, a detailed chemical kinetic model for the combustion of jet-fuel surrogate. The lumped model is validated against a large set of experimental data and for a wide range of conditions, for each *n*-alkane from *n*-pentane to *n*-dodecane with satisfactory results. The results obtained here further confirms the conclusion made in an early study that the cracking kinetics may be simplified. For practical fuels, such as JP-7 and JP-8, the cracking should lead to the production of a small number of relevant components, containing mostly hydrogen, methane and C₂-C₄ compounds. Thus, the alternative approach to understand the quantitative combustion behaviors of jet fuel seem to be feasible: the initial pyrolytic process of the fuel is described by a simplified model and the reaction kinetics of the cracked products is treated fundamentally. Further simplification of the fundamental H₂/CO/C₁-C₄ reaction model may be envisaged as well.

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