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Model Development and Reduction Methods for High-temperature Large Alkane Molecule Kinetics

Marcos Chaos, Andrei Kazakov, Zhenwei Zhao, Frederick L. Dryer

mchaos@princeton.edu

<http://www.princeton.edu/~combust>

Princeton University



Mechanical & Aerospace
Engineering Department

Introduction

There is continued interest in developing a better understanding of the pyrolysis and oxidation of large hydrocarbons which are representative of real fuels over a wide range of operating conditions. This is motivated by the need to improve the efficiency and emission of pollutant species from existing combustion systems as well as new engine/proposition designs that may use new fuels/surrogates (to represent more complex fuel-blended gasolines). To this end, robust chemical kinetics models and more accurate numerical tools are needed to improve our understanding of the complex physical and chemical processes taking place in combustion systems. Recognizing the problem of mechanistic complexity versus predictive robustness, this study aims to develop a partially reduced skeletal mechanism for large alkane molecules and the methodology is applied to *n*-hexadecane. Hexadecane is a primary reference fuel for cetane rating of diesel fuels and is a major component in simple mixtures used to emulate the autoignition and combustion behavior of distillate-type fuels utilized in advanced engine designs (e.g. direct injection and homogeneous charge compression ignition diesel engines). Models of this molecule [1, 2] are scarce and involve a large number of reactions and species which make them not readily applicable to the simulation of multi-dimensional fluid flow problems.

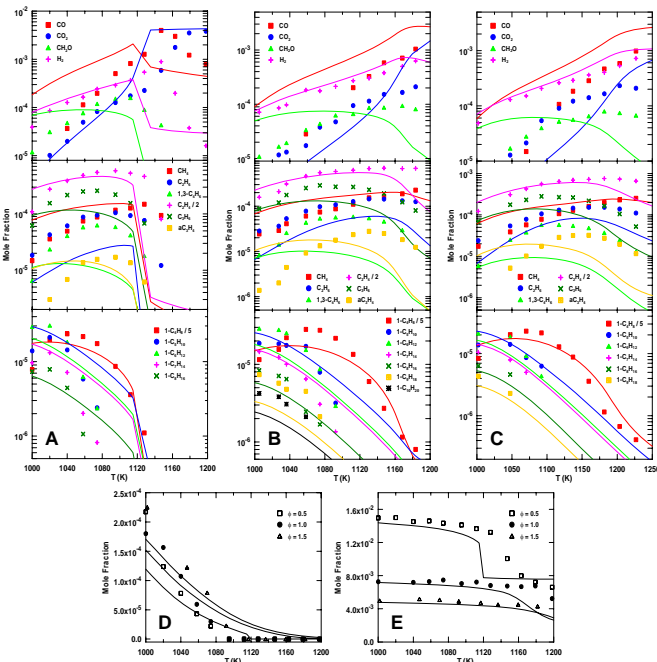


Figure 1. Comparison of experimental [2] and computed species profiles for the oxidation of hexadecane at atmospheric pressure in a Jet Stirred Reactor (JSR) with a mean residence time of 70 ms. (A) $\phi = 0.5$, 0.03% $C_{16}H_{34}$ / 1.47% O_2 / 98.5% N_2 ; (B) $\phi = 1.0$, 0.03% $C_{16}H_{34}$ / 0.735% O_2 / 99.235% N_2 ; (C) $\phi = 1.5$, 0.03% $C_{16}H_{34}$ / 0.49% O_2 / 99.48% N_2 ; (D) hexadecane consumption; (E) oxygen consumption.

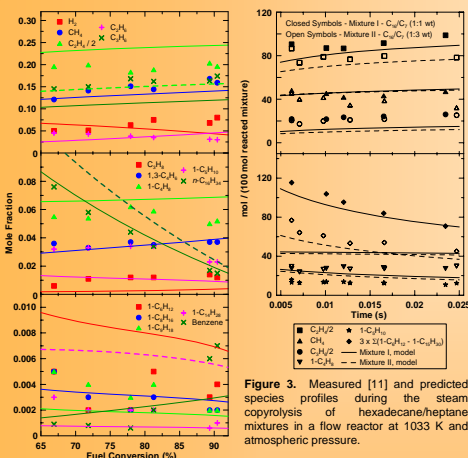


Figure 3. Measured [11] and predicted species profiles during the steam pyrolysis of hexadecane/heptane mixtures in a flow reactor at 1033 K and atmospheric pressure.

Figure 2. Experimental [10] and calculated species profiles during the steam pyrolysis of hexadecane at a temperature of 973 K and atmospheric pressure. Dashed lines are predictions using the model of Ristori et al. [2] (it is noted, however, that gas-oil is a complex mixture of a large number of paraffins, aromatics, and naphthas). Figures 2 and 3 compare computed species profiles against available data [10, 11] obtained during the thermal (steam) cracking of hexadecane and hexadecane/heptane mixtures at atmospheric pressure in quartz and stainless steel reactors, respectively. Reasonable agreement is observed for major species. Trends for large alkenes are also reproduced although it is noted that considerable experimental uncertainty exists for these measurements since the concentration of species larger than 1-pentene was very low. Of special importance are the alkane mixture results shown in Fig. 3 as only one extra species was added to the model (along with abstraction reactions following the rules in Table 1).

Pyrolysis: In industrial applications, alkenes are usually "manufactured" by pyrolysis of raw materials such as LPG and naphthas. In recent years, however, the use of higher-boiling materials has increased, especially gas-oil. Hexadecane kinetics studies are, thus, beneficial for these applications as the carbon content of gas-oil is similar to that of $C_{16}H_{34}$.

Oxidation: To date, the only detailed experimental study on the oxidation of hexadecane is that of Ristori et al. [2]. They studied the gas-phase oxidation of $C_{16}H_{34}$ in a Jet Stirred Reactor (JSR) at atmospheric pressure over 1000-1250K temperature range and for equivalence ratios spanning from 0.5 through 1.5. Concentration profiles were obtained for major and minor species (up to decene). Figure 1 shows the results obtained from the current model compared against the experimental data [2]. As can be seen, the model successfully captures reactivity trends as the equivalence ratio is varied. The model also predicts well the formation of alkenes. Some disparities exist in the prediction of CO and 1,3-butadiene. Such discrepancies have previously been reported [4, 9]; our laboratory is currently further refining the mechanism below the C_3 level in order to improve these results. The model, however, yields results comparable to the values obtained using the mechanism developed in [2] which consists of nearly 300 species and 1,800 reactions.

Validation

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Model Development

The current mechanism was built in a hierarchical manner. A high temperature hexadecane submechanism was combined with our recent update of the H_2/O_2 kinetic model [3] along with C_1-C_4 kinetics including the modifications listed in [4]. In the hexadecane submechanism, five classes of reactions are treated:

Table 1. H-atom abstraction rates. ($cm^3 \cdot mol^{-1} \cdot s^{-1}$)

Radical	Log (A/H)	b	E _a
Primary sites			
H	6.97	2.00	7.700
O	5.62	2.40	5.500
OH	6.37	1.80	974
HO ₂	3.90	2.55	16.500
CH ₃	11.34	0.00	11.600
O ₂	12.82	0.00	50.900
C ₂ H ₅	10.72	0.00	12.300
C ₂ H ₃	11.22	0.00	18.000
aC ₃ H ₇	11.12	0.00	20.500
Secondary sites			
H	6.64	2.00	5.700
O	4.76	2.60	1.769
OH (C-C-C)	5.70	2.00	-596
(-C-C-C)	5.47	2.00	-1.391
HO ₂	3.68	2.60	13.900
CH ₃	11.3	0.00	9.500
O ₂	13.3	0.00	47.590
C ₂ H ₅	10.10	0.00	10.400
C ₂ H ₃	11.30	0.00	16.800
aC ₃ H ₇	10.70	0.00	16.100

Olefin reactions: Olefins larger than C_4 follow unimolecular decomposition pathways as well as H abstraction (by H, O, OH, and CH_3) from primary, secondary and vinylic sites with subsequent rapid decomposition. Rates listed in [7] and [8] were used.

Model Reduction

An approach similar to that previously applied in our laboratory for *n*-decane [9] is extended here for *n*-hexadecane. The originally developed detailed mechanism (above) included detailed treatment of the alkyl radicals formed, incorporating both internal hydrogen isomerization and β -scission reactions and consisted of 151 species undergoing 1,155 reactions. In order to reduce the number of required species and simultaneously maintain the desired mechanistic detail, it was assumed that each of the alkyl radicals in the system exists in isomeric partial equilibrium above the C_4 level. Using the corresponding isomerization rates, the relative concentrations of each isomer within a given radical group were calculated as a function of temperature and an Arrhenius-type expression (i.e. $k = A T^b \exp(E_a/RT)$) was fitted to the results. The calculated Arrhenius parameters were used to modify the rates associated with the decomposition of each isomer radical. As a result, only a single radical species was needed to represent all the isomers associated with it and the respective reaction channels associated with each isomer. Using this approach, the resulting reduced model consisted of 98 species and 944 reactions.

Further Validation (Similarity to other Alkanes)

Despite the lack of experimental data (aside from the early work of Wagner and Dugger [12]), the current model was used to calculate laminar flame speeds of hexadecane/air mixtures at atmospheric pressure as this parameter is commonly used to partially validate kinetic models. It is expected, however, that hexadecane flame speeds will be very close to those of other linear alkanes since they share similar structures and flame temperatures (see Ref. 12) and, in fact, the current model shows this (Figure 4). The ability of the mechanism to accurately predict these flame speeds depends on the small-molecule kinetics as discussed in [4].

On the other hand, Horning et al. [14] reported that ignition times of *n*-alkanes (from C_3 up to C_{10}) exhibit similar pressure and oxygen concentration as well as activation energies. For qualitative purposes, the ignition delay of a stoichiometric mixture of $C_{16}H_{34}/O_2/Ar$ was calculated at atmospheric pressure over 1,300 < T < 1,500K. The apparent activation energy obtained from the calculation was approximately 44,000 cal/mol. This value compares well with the value reported by Horning et al. of 46,550 cal/mol.

Summary

A partially reduced skeletal reaction mechanism for the high temperature oxidation and pyrolysis of *n*-hexadecane has been developed consisting of 98 species and 944 reactions. By assuming that the alkyl radicals formed during these processes are in isomeric partial equilibrium, a considerable reduction in the required number of species was achieved while still maintaining the desired level of detail. The mechanism has been shown to reproduce the limited available experimental data and its performance is comparable to that of other much larger mechanisms available in the literature; furthermore, the model shows encouraging trends when considering other high temperature processes. The method described here can, thus, be successfully applied to the generation of compact mechanisms for other large alkanes found in modern fuels.

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