POLLUTANT FORMATION IN PREMIXED AND DIFFUSION FLAMES OF PARAFFINIC FUELS USING THE REDUCED UTAH SURROGATE MECHANISMS

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Introduction

Normal heptane, isooctane and cyclohexane have been the most interested surrogate components for liquid transportation and aviation fuels, due to their roles as indicative fuels for octane number and the representative compounds for normal, iso and cyclo-paraffins. Methodologies of mechanism generation for these representative fuel fractions have been discussed in detail in literature. The basics of fuel consumption in flames have been discussed by Vovelle[1], Ranzi[2], Zhang[3] and coworkers, among others. Ranzi et al.[2] presented a lumping technique that was also discussed in detail in an earlier study[3] and used for generation of reaction mechanisms that can be used to model flames of liquid fuels. The lumping approach is an effective reduction technique for models of large aliphatic fuels. Reaction pathway analysis presents another reduction technique that was used to reduce a complete kinetic set to smaller models. Doute et al.[4] reduced a n-decane model by removing less important reaction routes systematically and still obtained satisfactory agreement between the experimental data and predicted results. Bollig et al.[5] proposed a reduced n-heptane mechanism and modeled a diffusion flame with the emphasis on pollutant-related intermediates. The mechanism was further reduced using another technique with the assumption of partial equilibrium for intermediates.

There are many important applications that need reduced kinetic mechanism, especially in those that require expensive computations but are less demanding in kinetic details. For example, only a few dozen reactions can be comfortably acquired in aerodynamic applications. In this study, the detailed Utah Surrogate Mechanisms of about 1200 reactions and 210 species[3] will be reduced by a combined technique. The resultant mechanism will be used to simulate premixed and counter-flow diffusion flames of normal heptane, iso-octane and cyclo-hexane fuels. And the pollutant formation of soot precursors, e.g. benzene and acetylene, will be investigated for the three common surrogate components.

Experimental and Simulation Data

The premixed flames of normal heptane and iso-octane that were measured by El Bakali et al.[6] will be modeled during reduction and validation. The reduced Utah Surrogate Mechanisms will be also used to model a counter-flow diffusion flame with normal heptane[7], and predicted concentrations will be compared with measured profiles of these flames. All flames were operated at atmospheric pressure, and the fuel equivalence ratio for the premixed normal heptane and iso-octane flames is 1.9. The fuel vapor in the counter-flow diffusion flame is 15% normal heptane and 85% nitrogen at a cold gas velocity of 34.2 cm/s, and the oxidant is undiluted air with a velocity of 37.5 cm/s. Both the detailed (Version 3 β) and reduced Utah Surrogate Mechanisms will be used to model all three premixed flames. The simulator used was PREMIX of CHEMKIN IV.

Mechanism Reduction Methodology

The detailed Utah Surrogate Mechanism of about 1200 reactions and 210 species[3] will be reduced by a combination of several techniques for normal heptane and iso-octane fuels.

First, major fuel consumption pathways have been mapped out in an earlier study[3]. Paraffinic fuels are consumed by hydrogen abstraction, mainly with the most active abstractors H and OH radicals, and by thermal decomposition when fuel travels to high temperature region before being depleted by a rich radical pool, e.g. in diffusion flames. Therefore two fuel consumption classes were included in the reduced heptane mechanism, which is used as an example for the mechanism reduction procedure in this study.

Class 1: $C_7H_{16} + X_{H,OH,\ \&\ others} = C_7H_{15} + HX$
Class 2: $C_7H_{16} = \text{two alkyl radicals}$

There are three possible thermal decomposition reactions with a rupture of a C-C sigma bond: 1) $C_7H_{16} = C_4H_9\text{-}1 + C_3H_7\text{-}1$; 2) $C_7H_{16} = C_5H_{11}\text{-}1 + C_2H_5$; 3) $C_7H_{16} = C_6H_{13}\text{-}1 + CH_3$. The third reaction, however, will not be included in the reduced mechanism because the species C_6H_{13}-1 is not considered in order to reduce the number of species. The omission of the third reaction is justified in a reduced mechanism since it is a less important fuel decomposition route due to the stronger C-C sigma bond between the methyl and hexyl radicals. There are four different conjugate heptyl radicals, which were denoted by C_7H_{15}-1, C_7H_{15}-2, C_7H_{15}-3, and C_7H_{15}-4 in the detailed mechanism. Pitsch and coworkers[5] have proposed a lumping of heptyl species. The heptyl radicals are to be distinguished in this study only between the primary and secondary isomers by following the Pitsch proposal. Therefore, the generic rates proposed in the detailed mechanism[3] will be weighted by the six hydrogen atoms on the primary carbon atoms for the formation of PC_7H_{15}, and by ten other positions on the secondary carbon atoms for that of SC_7H_{15}.

The decomposition of conjugate heptyl radicals is represented by β scission that leads to a smaller alkyl radical and an olefin. All possible β scission reactions will be included in the reduction as if all conjugate heptyl radicals are distinguishable. In another word, the C_2-C_6 olefin formation will be considered in the following reactions.

R1: $PC_7H_{15} = C_2H_4 + C_5H_{11}\text{-}1$
R2: $SC_7H_{15} = C_3H_6 + C_4H_9\text{-}1$
R3: $SC_7H_{15} = C_4H_8\text{-}1 + C_3H_7\text{-}1$
R4: $SC_7H_{15} = C_6H_{12}\text{-}1 + CH_3$
R5: $SC_7H_{15} = C_5H_{10}\text{-}1 + C_2H_5$

The generic reaction rates used in the detailed mechanism, however, is no longer suitable for the reduced kinetics. It is clear that the lumped SC_7H_{15} species will have to be distributed into different product channels. A few kinetic factors need to be considered. First, different secondary heptyl radicals are formed unevenly from the fuel decomposition with a distribution of roughly 40/40/20% for the C_7H_{15}-2, C_7H_{15}-3, and C_7H_{15}-4 isomers, respectively, as a result of the symmetry factors of their formation. Also, the isomerization between heptyl radicals can change their formation rates by as much as 50%[8], with C_7H_{15}-3 gaining about 30-50% and C_7H_{15}-4 losing about 15-25%. Lastly, some reactions share a common precursor if distinguished, e.g. R3 and R4 for C_7H_{15}-3. Therefore, the formation of C_7H_{15}-2, C_7H_{15}-3, and C_7H_{15}-4 isomers is weighted by 36/50/14%, and the reactions R2-R5 are corrected by the secondary heptyl isomer distribution. This approach is an extension of the species lumping technique proposed by Pitsch and coworkers[5] since the isomerization effect is incorporated into the β scission decomposition rate in the current study. The isomerization between PC_7H_{15} and SC_7H_{15} isomers is also modified in order to reflect the reality that the lumped SC_7H_{15} species has a higher concentration than each of the C_7H_{15}-2, C_7H_{15}-3, and C_7H_{15}-4 isomers if distinguished. The isomerization from the secondary to the primary radicals in the detailed mechanism is dominated by C_7H_{15}-3 → C_7H_{15}-1 as the reaction was facilitated with a 6-membered pericyclic transition state. Therefore, the reaction rate of $SC_7H_{15} \rightarrow PC_7H_{15}$ was adjusted down by a factor of three to account for the concentration difference between SC_7H_{15} and C_7H_{15}-3 and other concerns in the difference of reaction barriers.

The smaller alkyl radicals formed from the fuel consumption decompose further via β scission, e.g. R6) $C_5H_{11}\text{-}1 = C_2H_4 + C_3H_7\text{-}1$; R7) $C_4H_9\text{-}1 = C_2H_4 + C_2H_5$; R8) $C_3H_7\text{-}1 = C_2H_4 + CH_3$. Olefin species are consumed by thermal decomposition that yields allyl or vinyl radicals and a smaller alkyl radical: R9) $C_6H_{12}\text{-}1 = CH_2CHCH_2 + C_3H_7\text{-}1$; R10) $C_5H_{10}\text{-}1 = CH_2CHCH_2 + C_2H_5$; R11) $C_4H_8\text{-}1 = CH_2CHCH_2 + CH_3$; R12) $C_3H_6 = CH_2CH + CH_3$. Abstraction reactions of propylene also contribute the consumption of the second abundant olefin: R13) $C_3H_6 + X\ (H, OH) = CH_2CHCH_2 + HX$.

The benzene formation in heptane flames was formulated in the reduced mechanism with the inclusion of the following two classes:

Class 3: $H_2CCCH + H_2CCCH = C_6H_6$
Class 4: $H_2CCCH + CH_2CCH_2 = C_6H_6 + H$
Class 5: $H_2CCCH + H_2CCCH = C_6H_5 + H$
$C_6H_5 + H = C_6H_6$

And benzene is consumed by the oxidation of phenyl radical by the following reactions: R14-15) $C_6H_6 + X\ (H, OH) = C_6H_5 + HX$; R16) $C_6H_5 + O_2 = C_6H_5O + O$; R17) $C_6H_5O = C\text{-}C_5H_5 + CO$; R18) $C_2H_3 + H_2CCCH = C\text{-}C_5H_5 + H$.

The reduced Utah Surrogate Mechanisms has a GRI core of C_1-C_2 hydrocarbons and $CO/CO_2/H_2/H_2O$ formation reactions. And the same reduction procedure has also been applied to the iso-octane and cyclo-hexane sub-mechanisms for their consumption pathways.

Reduced Mechanisms for Premixed Flames

The predicted concentrations using both the full and the reduced Utah Surrogate Mechanisms are compared with the measured profiles of selected species in **Figure 1** for the premixed normal heptane flame with an equivalence ratio of 1.9.

The predicted concentrations of most species are in satisfactory agreement with the experimental values by both the full and the reduced mechanisms. The results from the reduced mechanism match those from the full mechanism quite well for the fuel, oxidant and inert species. The predicted carbon dioxide profiles are almost identical as well between the two mechanisms. The reduced mechanism yields better water vapor concentrations. The predicted concentrations of olefins from ethylene to hexene using both mechanisms are in good agreement with the experimental profiles. In general, the reduced mechanism yields low concentrations than those obtained from the full mechanism. The deviation is desirable for the propylene and butylene profiles, which show almost perfect matches with measured profiles for both species.

The predicted concentrations of acetylenes and benzene using the full and the reduced mechanisms are in good agreement with the experimental measurements. The concentrations of propyne are over-predicted by both mechanisms with the reduced set yielding even higher profiles. In contrast, the predicted peak concentration of acetylene by the reduced mechanism is only 18% lower than the measured value. It is noted that the full mechanism yields a very close prediction of the peak acetylene concentration. The benzene source from C_2 + C_4 reactions are opted to be left out, which is estimated to account for 10-15% of the total benzene formation rate. The reduced formation rate, however, is counter-balanced by the omission of consumption routes to form phenol, toluene and other benzene derivatives. With the balanced benzene source and outlet routes, the resulting reduced mechanism yields very good benzene concentrations in comparison with the measured profile and that predicted by the full mechanism.

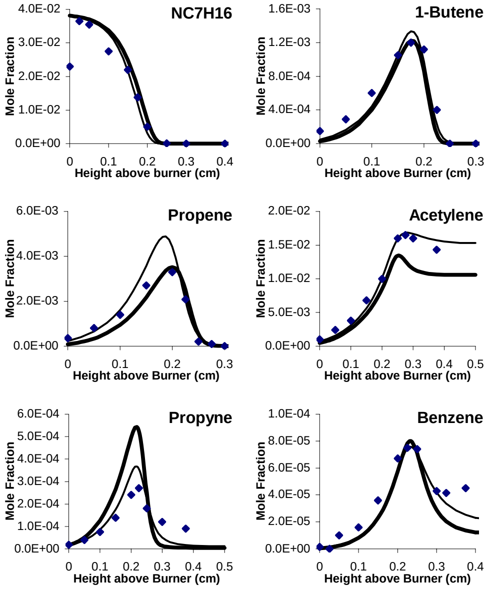

Figure 1. The predicted concentrations of selected species using the full Utah Surrogate Mechanism (light lines) and its reduced mechanism (heavy lines) are compared with the measured profiles (symbols) for the premixed n-heptane flame (ϕ =1.9).

The predicted profiles of selected species of chemical classes using both mechanisms are compared with the experimental data in **Figure 2** for the premixed iso-octane flame. In general, the reduced mechanism yields as good results as the full mechanism. Especially, the predicted concentrations of propyne and acetylene are better than those obtained from the full mechanism.

Reduced Mechanisms for the Diffusion Flame

The predicted concentrations of selected species in the counter-flow diffusion n-heptane flame using the reduced mechanisms are compared with the experimental data in **Figure 3**. The reduced mechanism yields very good results for the profiles of reactants and products. The largest deviations for the maximum concentrations of major species are seen in the profiles of H_2 (+37%) and CO (+19%), which are not shown in **Figure 3**. The simulated results present a perfect match for the profiles of propylene, and acetylene and ethylene that was reported as the sum of the two C_2 species in the experiment. The measured profile of C_6 species is compared with the sum of the concentrations of 1-hexene and benzene, the two most abundant C_6 species in the gas phase. The reduced mechanism over-predicts the total C_6 species concentrations by about 50%.

Acetylene and Benzene Production Potential

The formation potential of benzene and acetylene was examined in an earlier study[3] for surrogate components of normal, iso, cyclo-paraffins, and aromatics in a premixed kerosene flame. A similar calculation was carried out for the normal heptane, iso-octane and cyclo-hexane fuels in the current study, in order to generalize the formation potential of the most abundant soot precursors, i.e. acetylene and benzene, in diffusion flames. To this end, three modeled flames were converged using the reduced Utah Surrogate Mechanisms under the same experimental conditions but with single fuels of normal heptane, iso-octane and cyclo-hexane. The predicted concentrations of benzene and acetylene in three modeled flames are compared with each other in **Figure 4**.

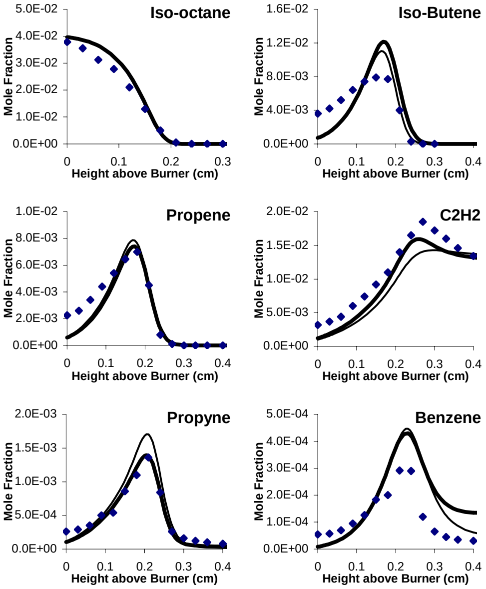

Figure 2. The predicted concentrations of selected species using the full Utah Mechanism (light lines) and its reduced mechanism (heavy lines) are compared with the measured profiles (symbols) for the premixed iso-octane flame (ϕ =1.9)

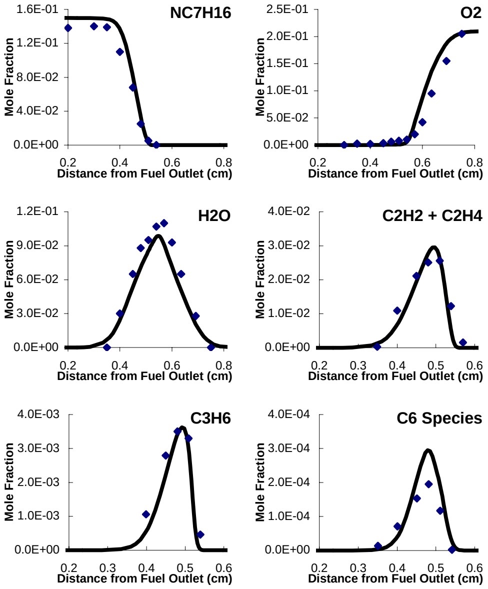

Figure 3. The predicted concentrations of selected species using the full Utah Mechanism (light lines) and its reduced mechanism (heavy lines) are compared with the measured profiles (symbols) for the counter-flow diffusion n-heptane flame.

It is noted that acetylene and benzene have significant concentrations only at the fuel side of the flame front. The relative benzene formation potential among three fuels follows the order that was also identified in the premixed flames[3]: normal < iso < cyclo paraffins. The order reflects the chemical structural features of the fuels. For example, the cascading dehydrogenation of the cyclo-hexane fuel, i.e. cyclo-hexane → cyclo-hexene → cyclo-hexadiene → benzene, is a more direct pathway for the benzene formation, in comparison with combination reactions in normal heptane and iso-octane flames. Therefore, the cyclo-hexane flame yields the highest benzene concentrations. The preferential formation of iso-butylene also reflects the uniqueness of structural characteristics of iso-octane. The abundant iso-butylene presence in the gas phase leads to a larger population of propylene, which can be hydrogen abstracted to form the most important benzene precursors, i.e. propargyl radical and allene. It is noteworthy that the difference in the benzene formation potential is less dramatic than that observed in premixed flames, which can be as high as one order of magnitude between normal and cyclo paraffinic fuels.

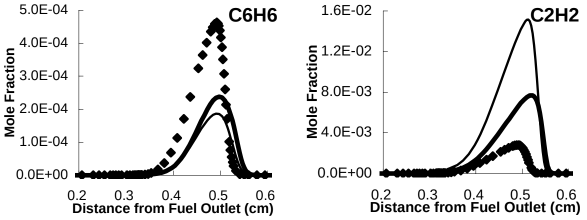

Figure 4. The predicted concentrations of benzene (left) and acetylene (right) using the full Utah Surrogate Mechanisms show formation trends for n-heptane (light lines), iso-octane (heavy lines) and cyclo-hexane (symbols) fuels in counter-flow diffusion flame.

The acetylene formation potential is also structural dependent but follows the reverse order seen for benzene: cyclo < iso < normal paraffins. It is noted that the reduced cyclo-hexane mechanism yields underestimated acetylene concentrations by a factor of two. If the relative deviation is also a good estimation in diffusion flames, the yield from cyclo-hexane flame is still lower than that from the iso-octane flame. In contrast, the acetylene production potential is very similar for normal, iso, and cyclo-paraffins in the premixed flame[3].

Conclusion

The detailed Utah Surrogate Mechanisms was reduced to a 48-species 138-reaction mechanism using a combination of techniques. The resultant mechanism yields satisfactory predictions for species concentrations in one counter-diffusion and three premixed flames burning normal heptane, iso-octane and cyclo-hexane fuels. Fuel structural properties were found to be critical for the benzene formation in both premixed and diffusion flames.

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