Technical Notes

Joint Jet-A/Silane/Hydrogen Reaction Mechanism

Mark J. Lewis* and Jee Su Chang[†]
University of Maryland,
College Park, Maryland 20742-3015

Introduction

HYDROGEN has been studied extensively as the fuel of choice for scramjet engines because of its high specific energy, good cooling capacity, and rapid combustion rate.[1] There would, however, be advantages to using hydrocarbon fuel in a scramjet. Despite their lower heats of reaction, hydrocarbon fuels have densities that are over 10 times higher than liquid hydrogen, allowing for greater vehicle volumetric efficiencies than hydrogen. They are also simpler to handle and are compatible with current fleet supplies. Because of this promise, hydrocarbon combustion for scramjets has been explored in some detail, including the work of Edwards.[2] Unfortunately, hydrocarbon fuels ignite more slowly than hydrogen under similar inlet conditions, thus requiring longer combustor sections. This, in turn, may increase the required vehicle weight and the viscous drag losses. One method for decreasing reaction time is to use a piloting additive. To understand the benefits and tradeoffs associated with piloting a hydrocarbon scramjet, including impact on combustor length, reaction efficiency, and specific impulse, it is useful to have a simple yet complete reaction mechanism, suitable for inclusion in computational studies. As such, a joint chemical kinetic reaction mechanism is presented here for studying the combustion properties of one particular hydrocarbon jet fuel, Jet-A, with silane and/or hydrogen piloting.

Assembled Reaction Mechanism

Three separate published chemical kinetic reaction mechanisms for hydrogen, silane, and Jet-A fuel were used to assemble the present mechanism. The combined mechanism was partially validated by having it reproduce the experimental data and the separate reactions of the original mechanisms. The individual mechanisms were chosen from among the available models to be anchored in experimental results and to include a manageable number of reactions and species. The hydrogen mechanism selected for use in this combined mechanism is that of Jachimowski,[3] which has already been proven against experimental data in modeling combustion in hydrogen scramjet engines. The silane mechanism chosen for this work is that of McLain et al.,[4] derived from ignition tests of silane and methane combustion. This silane mechanism was deemed more applicable to the current problem than previous mechanisms that focused on ignition enhancement of hydrogen with silane. The Jet-A mechanism used in this work is that of Kundu et al.,[5] chosen in part because it contains only 23 reactions and is, therefore, computation-

ally benign. More complete mechanisms are available such as the comprehensive mechanism of Maurice,[6] which is a general model for a wide variety of aviation fuels, but includes over 1000 reactions.

The assembled Jet-A/silane/hydrogen mechanism is listed in Table 1 and consists of 58 reactions of 25 species. It is derived from reactions 1–3 and 13–23 of the Jet-A mechanism,[5] reactions 25–48 of the silane mechanism,[4] and reactions 1–20 of the hydrogen mechanism.[3] Redundant reactions were replaced. The forward rates are in three-parameter form, as in Eq. (1):

$$k_f = A_a T^n e^{-E_a/R_u T} [X]^a [Y]^b [Z]^c \qquad (1)$$

The exponents a, b, and c are the coefficients of the corresponding species in the reaction except for reactions 1–3, where the values are noted beneath the equations and are derived from the original reference.[5]

Reaction Mechanism Verification

The mechanism was included in Chemkin-II from Sandia National Laboratories, for calculation of properties and reaction rates.[7]
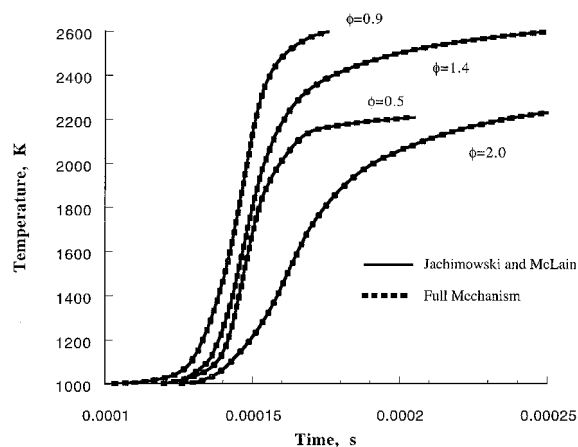
Fig. 1 Comparison of present mechanism with original mechanism for hydrogen reaction at four different equivalence ratios, for 1 atm and 1000 K initial conditions. Both mechanisms produce identical results within computational accuracy.
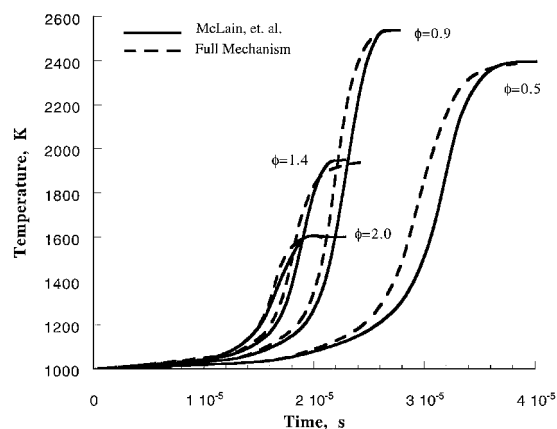
Fig. 2 Comparison of present mechanism with original mechanism for silane reaction at four different equivalence ratios, for 1 atm and 1000 K initial conditions.

Table 1   25 species, 58 reaction Jet-A/silane/hydrogen reaction mechanism

	Reaction	A, mole-cm-s-K units	n	E_a, cal/mole	Reference
1	$C_{12}H_{23} + \{N_2\} \rightarrow 12CH + 11H + \{N_2\}$ $a = 0.8\ b = 0.8$	$4.35e9$	0	30,000	Kundu et al.[5]
$2_{forw.}$	$H_2 + N_2 + \{CH\} \rightarrow \{CH\} + 2NH$ $a = 0.1\ b = 1.0\ c = 2.0$	$1e15$	0	78,000	Kundu et al.[5]
$2_{back.}$	$\{CH\} + 2NH \rightarrow H_2 + N_2 + \{CH\}$ $a = 2.0\ b = 2.0$	$1.95e15$	0	0	Kundu et al.[5]
$3_{forw.}$	$\{O\} + N_2 + HO_2 \rightarrow 2NO + H + \{O\}$ $a = 0.1\ b = 0.5\ c = 1.0$	$1.6e9$	0.5	43,900	Kundu et al.[5]
$3_{back.}$	$2NO + H \rightarrow N_2 + HO_2$ $a = 1.1\ b = 1.0$	$2.5e10$	0	8,000	Kundu et al.[5]
4	$CO + OH \rightleftharpoons CO_2 + H$	$1.51e7$	1.28	-758	Kundu et al.[5]
5	$N_2 + 2CH \rightleftharpoons C_2H_2 + N_2$	$1.5e17$	0	-758	Kundu et al.[5]
6	$C_2H_2 + O_2 \rightleftharpoons 2CO + H_2$	$3e15$	0	19,000	Kundu et al.[5]
7	$CH + OH \rightleftharpoons CO + H_2$	$3e13$	0	6,000	Kundu et al.[5]
8	$CH + O \rightleftharpoons CO + H$	$3e12$	0.6	0	Kundu et al.[5]
9	$CH + NO \rightleftharpoons NH + CO$	$1e11$	0	0	Kundu et al.[5]
10	$N_2 + O \rightleftharpoons N + NO$	$9e13$	0	75,000	Kundu et al.[5]
11	$N + O_2 \rightleftharpoons NO + O$	$6.3e9$	1	6,300	Kundu et al.[5]
12	$NO + H \rightleftharpoons N + OH$	$1e12$	0	48,000	Kundu et al.[5]
13	$NH + O \rightleftharpoons NO + H$	$2.5e4$	2.64	0	Kundu et al.[5]
14	$NH + NO \rightleftharpoons N_2 + OH$	$2e15$	-0.8	0	Kundu et al.[5]
15	$SiH_4 \rightleftharpoons SiH_2 + H_2$	$3.3e12$	0	51,090	McLain et al.[4]
16	$SiH_4 + O_2 \rightleftharpoons SiH_3 + HO_2$	$2e11$	0	44,000	McLain et al.[4]
17	$SiH_4 + HO_2 \rightleftharpoons SiH_3 + H_2O_2$	$3e12$	0	5,600	McLain et al.[4]
18	$SiH_4 + H \rightleftharpoons SiH_3 + H_2$	$1.5e13$	0	2,500	McLain et al.[4]
19	$SiH_4 + O \rightleftharpoons SiH_3 + OH$	$4.2e12$	0	1,600	McLain et al.[4]
20	$SiH_4 + OH \rightleftharpoons SiH_3 + H_2O$	$8.4e12$	0	100	McLain et al.[4]
21	$H + SiH_3 \rightleftharpoons SiH_2 + H_2$	$1.5e13$	0	2,500	McLain et al.[4]
22	$O + SiH_3 \rightleftharpoons SiH_2O + H$	$1.3e14$	0	2,000	McLain et al.[4]
23	$OH + SiH_3 \rightleftharpoons SiH_2O + H_2$	$5e12$	0	0	McLain et al.[4]
24	$SiH_3 + O_2 \rightleftharpoons SiH_2O + OH$	$8.6e14$	0	11,430	McLain et al.[4]
25	$SiH_2 + O_2 \rightleftharpoons SiHO + OH$	$1e14$	0	3,700	McLain et al.[4]
26	$SiH_2O + M \rightleftharpoons SiHO + H + M$	$5e16$	0	76,600	McLain et al.[4]
27	$SiH_2O + H \rightleftharpoons SiHO + H_2$	$3.3e14$	0	10,500	McLain et al.[4]
28	$SiH_2O + O \rightleftharpoons SiHO + OH$	$1.8e13$	0	3,080	McLain et al.[4]
29	$SiH_2O + OH \rightleftharpoons SiHO + H_2O$	$7.5e12$	0	170	McLain et al.[4]
30	$SiH_2O + HO_2 \rightleftharpoons SiHO + H_2O_2$	$1e12$	0	8,000	McLain et al.[4]
31	$SiHO + M \rightleftharpoons SiO + H + M$	$5e14$	0	29,000	McLain et al.[4]
32	$SiHO + H \rightleftharpoons SiO + H_2$	$2e14$	0	0	McLain et al.[4]
33	$SiHO + O \rightleftharpoons SiO + OH$	$1e14$	0	0	McLain et al.[4]
34	$SiHO + OH \rightleftharpoons SiO + H_2O$	$1e14$	0	0	McLain et al.[4]
35	$SiHO + O_2 \rightleftharpoons SiO + HO_2$	$1.2e14$	0	3,975	McLain et al.[4]
36	$SiO + OH \rightleftharpoons SiO_2 + H$	$4e12$	0	5,700	McLain et al.[4]
37	$SiO + O + M \rightleftharpoons SiO_2 + M$	$2.5e15$	0	4,370	McLain et al.[4]
38	$SiO + O_2 \rightleftharpoons SiO_2 + O$	$1e13$	0	6,500	McLain et al.[4]
39	$H_2 + O_2 \rightleftharpoons 2OH$	$1.7e13$	0	48,000	Jachimowski et al.[3]
40	$H + O_2 \rightleftharpoons OH + O$	$2.6e14$	0	16,800	Jachimowski et al.[3]
41	$O + H_2 \rightleftharpoons OH + H$	$1.8e10$	1	8,900	Jachimowski et al.[3]
42	$OH + H_2 \rightleftharpoons H_2O + H$	$2.2e13$	0	5,150	Jachimowski et al.[3]
43	$2OH \rightleftharpoons H_2O + O$	$6.3e12$	0	1,090	Jachimowski et al.[3]
44	$H + OH + M \rightleftharpoons H_2O + M$	$2.2e22$	-2	0	Jachimowski et al.[3]
45	$2H + M \rightleftharpoons H_2 + M$	$6.4e17$	-1	0	Jachimowski et al.[3]
46	$H + O + M \rightleftharpoons OH + M$	$6e16$	-0.6	0	Jachimowski et al.[3]
47	$H + O_2 + M \rightleftharpoons HO_2 + M$	$2.1e15$	0	$-1,000$	Jachimowski et al.[3]
48	$HO_2 + H \rightleftharpoons H_2 + O_2$	$1.3e13$	0	0	Jachimowski et al.[3]
49	$HO_2 + H \rightleftharpoons 2OH$	$1.4e14$	0	1,080	Jachimowski et al.[3]
50	$HO_2 + H \rightleftharpoons H_2O + O$	$1e13$	0	1,080	Jachimowski et al.[3]
51	$HO_2 + O \rightleftharpoons O_2 + OH$	$1.5e13$	0	950	Jachimowski et al.[3]
52	$HO_2 + OH \rightleftharpoons H_2O + O_2$	$8e12$	0	0	Jachimowski et al.[3]
53	$2HO_2 \rightleftharpoons H_2O_2 + O_2$	$2e12$	0	0	Jachimowski et al.[3]
54	$H + H_2O_2 \rightleftharpoons H_2 + HO_2$	$1.4e12$	0	3,600	Jachimowski et al.[3]
55	$O + H_2O_2 \rightleftharpoons OH + HO_2$	$1.4e13$	0	6,400	Jachimowski et al.[3]
56	$OH + H_2O_2 \rightleftharpoons H_2O + HO_2$	$6.1e12$	0	1,430	Jachimowski et al.[3]
57	$H_2O_2 + M \rightleftharpoons 2OH + M$	$1.2e17$	0	45,500	Jachimowski et al.[3]
58	$2O + M \rightleftharpoons O_2 + M$	$6e17$	0	$-1,800$	Jachimowski et al.[3]

The VODPK routine was used to integrate the set of stiff equations governing the chemical reactions and the properties of the flow.[8] The Chemkin-II thermodynamic database[9] was used for most chemical species, with additions for silane species (SiH_2O, $SiHO$, SiO, and SiO_2) and Jet-A.[10]

Comparisons were made using the complete mechanism and the original mechanisms from which it was assembled at varying equivalence ratios. A constant pressure model was used to simulate a well-stirred reactor for these comparisons. Figure 1 shows the comparison of the present mechanism with the hydrogen mechanism; the results are identical within plotting accuracy. The initial conditions chosen for this comparison were 1 atm and 1000 K at four equivalence ratios, representative values for supersonic combustion. Figure 2 shows the comparison of the present mechanism with the original silane mechanism. Though not identical, the ignition delay times are very close, as are the final temperatures. Figure 3 shows
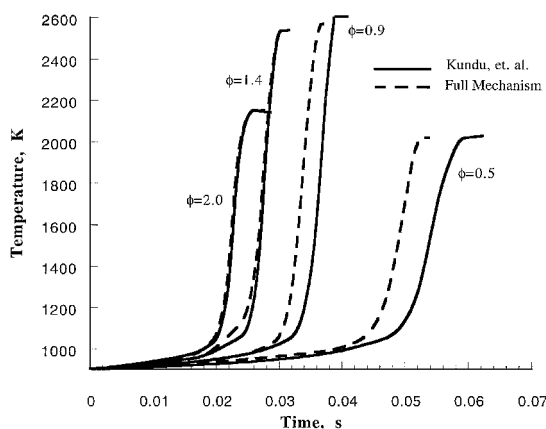
Fig. 3 Comparison of present mechanism with original mechanism for Jet-A reaction at four different equivalence ratios, for 1 atm and 1000 K initial conditions.
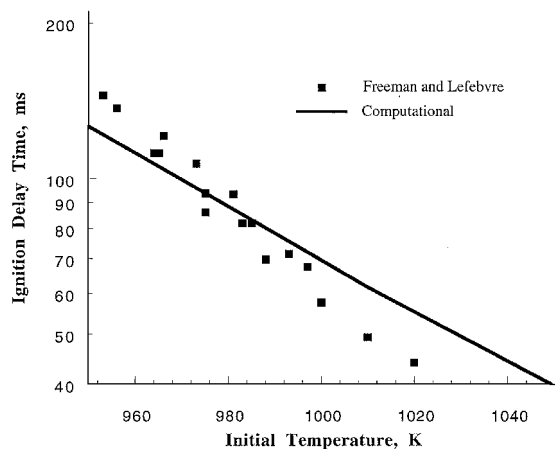

Fig. 4 Comparison of ignition delay time for Jet-A fuel at $\phi = 0.5$, 1 atm measured by Freeman and Lefebvre,[9] and the computational reaction mechanism, as a function of initial temperature.

the comparison of the present reaction mechanism and the original Jet-A mechanism. There is at most a 10% difference in the ignition delay time and a 5% difference in the final temperature between the present mechanism and the original. The present mechanism has also been matched to experimental data sets; each of the individual mechanisms cited has itself been validated, and the overall ignition delay time from the combined set has been compared to the data of Freeman and Lefebvre,[11] as shown in Fig. 4. Note that differences between the calculated ignition delay and experimental results are likely due to inconsistencies in defining that parameter: The experimental determination was done by visually locating a sudden pressure rise, whereas the computational result was set by a 20% temperature rise.[12]

Conclusions

A joint Jet-A/silane/hydrogen reaction mechanism has been constructed from existing mechanisms for modeling the combustion of Jet-A with silane as a pilot igniter. This model can now be used for studies of hydrocarbon combustor length and reaction efficiency, as a guide for design tradeoffs, and for experimental studies. For instance, a quasi-one-dimensional scramjet combustor model was implemented that included this present mechanism, from which it was shown that the addition of silane is indeed beneficial in decreasing the combustor length in a scramjet engine (though depending on the added fraction, specific impulse can suffer because of the reduced average heat of reaction).[12] At 1 atm, 1000 K, the characteristic reaction lengths for a hydrocarbon scramjet with 0.5 equivalence ratio and Mach 3 entrance conditions can be reduced from approximately 100 m with no piloting to 0.1 m with 20% silane addition. With 10% silane, the characteristic reaction length is approximately 1.2 m. However, the effective specific impulse for that combustor (calculated from the difference between maximum available thrust

and total vehicle drag) will drop from 550 s without silane to 400 s with 10% silane and to less than 300 s with 20% silane.

References

[1]Lewis, M., and Gupta, A., "Impact of Fuel Selection on Hypersonic Vehicle Optimization," International Society for Air Breathing Engines, Paper 97-7200, Sept. 1997.

[2]Edwards, T., "Combustion Challenges of High Temperature Jet Fuels," American Inst. of Chemical Engineers, AIChE Annual Meeting, Chicago, IL, Paper 204a, Nov. 1996.

[3]Jachimowski, C. J., "An Analytical Study of the Hydrogen–Air Reaction with Application to Scramjet Combustion," NASA TP-2791, Feb. 1988.

[4]McLain, A. G., Jachimowski, C. J., and Rogers, R. C., "Ignition of Mixtures of SiH_4, CH_4, O_2, and Ar or N_2 Behind Reflected Shock Waves," NASA TP-2415, April 1985.

[5]Kundu, K. P., Penko, P. F., and Yang, S. L., "Reduced Reaction Mechanisms for Numerical Calculations in Combustion of Hydrocarbon Fuels," AIAA Paper 98-0803, Jan. 1998.

[6]Maurice, L. Q., "Detailed Chemical Kinetic Models for Aviation Fuels," Ph.D. Thesis, Univ. of London, London, Oct. 1996.

[7]Kee, R. J., Rupley, F. M., and Miller, J. A., "Chemkin-II: A Fortran Chemical Kinetics Package for the Analysis of Gas Phase Chemical Kinetics," SAND89-8009B, Sandia National Labs., Albuquerque, NM, April 1989, URL: http://www.nist.gov/cstl/div836/ckmech.

[8]"VODPK Routine," Netlib Repository, URL: http://www.netlib.org.

[9]Kee, R. J., Rupley, F. M., and Miller, J. A., "The Chemkin Thermodynamic Database," SAND87-8215B, Sandia National Labs., Albuquerque, NM, March 1990.

[10]Gracia-Salcedo, C. M., Brabbs, T. A., and McBride, B. J., "Experimental Verification of the Thermodynamic Properties for a Jet-A Fuel," NASA TM-101475, Sept. 1988.

[11]Freeman, G., and Lefebvre, A. H., "Spontaneous Ignition Characteristics of Gaseous Hydrocarbon–Air Mixtures," Combustion and Flame, Vol. 58, No. 2, Nov. 1984, pp. 153–162.

[12]Chang, J. S., and Lewis, M. J., "Development of a Jet-A/Silane/Hydrogen Reaction Mechanism for Modeling a Scramjet Combustor," AIAA Paper 99-2252, presented at the 1999 AIAA/ASME/SAE Joint Propulsion Conf., Los Angeles, CA, June 1999.

Lithium Peroxide Fuel Cells for Electric Vehicle Propulsion

Gautum Agarwal*
*National Institute for Aviation Research,
Wichita, Kansas 67260*

Introduction

A PROPULSION system consisting of a compact electric motor and one or more lithium-based fuel cells (Li–water, Li–hydrogen peroxide, Li–air) holds considerable promise as a nonpolluting, recyclable-fuel power plant for airplanes, uncrewed air vehicles (UAV), helicopters, automotive vehicles, and surface water vehicles. The technology has its roots in U.S. Navy electric torpedo research done in the 1970s by Lockheed (see Refs. 1–3) and subsequent classified Defense Advanced Research Projects Agency-sponsored research in the 1980s for an uncrewed reconnaissance aircraft.

Recent studies[4] have shown that the gasoline-fueled propulsion system of a typical 225-hp light airplane could be replaced with an electric-motor, lithium–air fuel cell power plant developing the same power and the same endurance with approximately the same weight. The by-product of producing electricity in the fuel cell is lithium hydroxide (Li–OH), which would be retained onboard and recycled after flight to retrieve the metallic lithium for reuse. Furthermore,