13

O_2/CH_4 Kinetic Mechanisms for Aerospace Applications at Low Pressure and Temperature, Validity Ranges and Comparison

Angelo Minotti
"Sapienza" University of Rome, Italy

1. Introduction

In recent years, the propellant combination Ox/CH_4 has received attraction in Japan, USA and Europe as a propellant combination for attitude control, upper stage, booster engines and microcombustion systems. Moreover, this propellant pair is of interest for exploration missions (Stone et al., 2008; Hulbert et al., 2008; Arione, 2010; Kawashima et al., 2009) and for in-space propulsion systems. The reason of the exploration/in-space interest stays in the fact that all the missions with a reduced requirement of thermal management and propellant losses through evaporation will surely profit from a Ox/CH4 based propulsion system. Microcombustion, for space and terrestrial use, takes profit from the Ox/CH4 propellant combination thanks to its availability, easy to handle, and knowledge. Besides the interest in methane for space-terrestrial applications, this propellant being a renewable bio-fuel has seen rising interest for both economic and ecologic reasons.

Microthrusters were associated with the emergence of micro- and nano-satellite concepts, in which satellites are conceived capable of the same or similar performance of conventional satellites within a much smaller package/weight by using MEMS technology (Micro Electrical Mechanical System). This increasing interest in MEMS devices, in particular those based or including combustion/chemical propulsion, is also forcing new needs and problems to emerge (Janson, 1994; DeGroot & Oleson, 1996; Mueller, 1997; Bruno, 2001). One of these is the heat loss through combustor walls due to the much increased surface/volume ratio reducing the actual energy available for the cycle chosen: this explains the sometimes startlingly low temperatures observed experimentally (Minotti et al., 2009; Bruno, 2001; Cozzi, 2007; Cozzi & Caratti, 2007; Bruno et al., 2003; Cozzi et al., 2007). Even when equivalence ratios (Φ) are close to one, these call for kinetics capable of realistically predicting ignition delays times and combustion efficiency at a reasonable computational cost.

The requirement to predict with sufficient accuracy combustion performance and heat load to the chamber walls has lead, in the last decade, the numerical modelling to rapidly become an essential part of combustion research and development programs, and there has been an accelerating evolution from the use of single-step empirical kinetics, to the use of lumped semiglobal (multistep) models (Wesbrook & Dryer, 1981; Bowman, 1986), and finally to the inclusion of full detailed chemical kinetic mechanisms to better simulate chemistry interactions. In addition, detailed mechanisms have been developed and validated for the

simplest fuel molecules (Westbrook and Dryer, 1981) and are not available for most practical fuels. Finally there are many occasions where the great amount of chemical information produced by a detailed reaction mechanism is not necessary and a simple mechanism will suffice together with the fact that 3D combustors cannot easily include detailed kinetic mechanisms because the computational costs of such a treatment would be much too great.

Several works concerning hydrocarbon kinetics are present in literature (Paczko et al., 1988; Westbrook Dryer, 1981; Kee et al., 1985; Heffington, 1997; Hautman, 1981; Trevino & Mendez, 1992; Dagaut, 1991), and the work of Gardiner (1999) is important to understand the hydrocarbon oxidation chemistry, in particular for what concerns differences between methane and other hydrocarbons. The state of the art for methane reactions is by the Gas Research Institute, periodically releasing new updated versions of its detailed methane-air reaction mechanism (GRI-Mech, http://www.me.berkeley.edu/gri_mech/ or http://www.gri.org).

Said that, this work indicates two ways to "define/build" a reaction mechanism and presents five reaction mechanisms adopted in hydrocarbons simulations: one global, two 2-steps, one multisteps and one detailed reaction mechanism.

All of them are compared with the detailed GRI-Mech3.0 reaction mechanism (GRI-Mech, 1999) by means of the CHEMKin3.7 tool (the Aurora application) to figure out the ignition delay time and final temperature differences, in order to understand the problems, and limits, related to a delicate topic as the reaction mechanism modelling is.

Section 2 provides few important hints to define a reaction mechanism, section 3 shows the five reaction mechanisms which are studied, while section 4 and 5 report comparisons and their validity ranges.

2. Reaction mechanism definition

A reaction mechanism may be obtained following, in general, two different paths, depending on whether a reduced mechanism or a semiglobal mechanism is required.

If a reduced mechanism is the goal, the "recipe" might be summarized by:

1. definition of the starting detailed mechanism;
2. definition of the operating conditions;
3. sensitivity analysis to reduce the reactions number.

(The sensitivity $\left(Y'_{X_i}\right)$ analysis is the study of how the variation (uncertainty) in the output (Y) of a mathematical model can be apportioned, qualitatively or quantitatively, to different sources (X_i) of variation in the input of a model, that is $Y'_{X_i} = \frac{\partial Y}{\partial X_i}$; this measure tells how sensitive the output is to a perturbation of the input. If a measure independent from the units used for Y and X_i is needed, $S^r_{X_i} = \left(\frac{\bar{X}_i}{\bar{Y}}\right)\left(\frac{\partial Y}{\partial X_i}\right)$ can be used, where $\bar{X}_i$ is the nominal (or central, if a range is known) value of factor X_i and $\bar{Y}$ is the value taken by Y when all input factors are at their nominal value. In the reaction mechanisms the sensitivity analysis is carried out analysing the sensitivity of some species or of some reaction velocities on the overall mechanism).

On the other hand, if a semiglobal mechanism is the goal, the "recipe" might be summarized in the following way:

1. definition of species of interest (they affect the reaction enthalpy and then the final temperature);

2. definition of reactions (and their number);
3. definition of operating conditions;
4. modification of Arrhenius variables (A, n and E_a) to obtain the required ignition delay.

Any simplified reaction mechanism must be capable of reproducing experimental flame properties over the range of operating conditions under consideration. Hence, in both the paths the operating conditions definition plays a fundamental rule; they must be previously decided because the chemistry model, as every model, has a narrow range of validity and fits real data in a narrow range. It is not uncommon that models which fit data just in some points are adopted, by means of extrapolation laws, to figure out chemistry behaviours in ranges wider than their original validity without highlighting the errors percentage differences in these new ranges. Unfortunately this operation leads to big mistakes which are often neglected.

Experience shows, and this will be clear in the following sections, that most or almost all reduced mechanisms are tuned to predict data at *high* temperatures (where it is easy to obtain accurate data) but often at low temperatures, and low pressure, (i.e. 1000K-2000K and for pressures in the range between 1atm and 5atm, typical of non-adiabatic combustion) they are not accurate or do not predict ignition at all.

In general, for a semiglobal mechanism, the simplest overall reaction representing the oxidation of a conventional hydrocarbon fuel is:

$$Fuel \; + \; n_1 O_2 + \left(3.76 N_2\right) \rightarrow n_2 CO_2 + n_3 H_2 O + \left(n_1 3.76 N_2\right)$$

where n_i are determined by the choice of fuel.

This global reaction is often a convenient way of approximating the effects of the many elementary reactions which actually occur but it overestimates the final temperature and mispredicts the overall reaction rate.

The rate expression of the single reaction is usually expressed by:

$$k_{ov} = A T^n \exp\left(-\frac{E_a}{RT}\right)\left[Fuel\right]^a \left[Oxider\right]^b$$

where:

- A is the frequency factor which depends on how often molecules collide when all concentrations are 1mol/L and on whether the molecules are properly oriented when they collide;
- E_a is the energy that must be overcome for a chemical reaction to occur (kJ/mole);
- n defines the functionality rate law with temperature;
- a and b define the functionality rate law with fuel and oxider mass fractions;

This rate must therefore represent an appropriate average of all of the individual reaction rates involved during the reaction and this is obtained tuning the A, E_a, n, a and b variables.

3. Reaction mechanisms

The reaction mechanisms presented here are:

1. Westbrook and Dryer: 4 species and 1 reaction (Westbrook & Dryer, 1981);
2. Westbrook and Dryer: 5 species and 2 reactions (Westbrook & Dryer, 1981);
3. Minotti: 6 species and 2 reactions (Minotti et al., 2009);
4. Kee: 17 species and 58 reactions (Kee et al., 1985);

5. GRI-Mech 12: 32 species and 177 reactions (Gri-Mech 1.2, 1994; Heffington et al., 1997);

These mechanisms have been compared to the predictions given by the detailed GRI-Mech 3.0 (53 species and 325 reactions (GRI-Mech 3.0, 1999; Dagaut et al., 1991)), assumed as the "*reference model*" , for a wide range of equivalence ratio ($0.3 \leq \Phi \leq 1.9$), and at three different pressures (P=1, 3 and 5 atm).

In the following sections the ignition delay comparison and the final temperature comparison are respectively reported.

4. Comparisons – ignition delay times

The ignition delay time is the elapsed time to obtain a temperature increase, from the injection temperature, of 400K.

The ignition delay time has been compared among the five mechanisms, listed above, adopting reactants in the temperature range 1000K - 2000K and at pressure 1, 3 and 5atm. The equivalence ratio (Φ) range tested was from Φ=0.3 to Φ=1.9 (ΔΦ=0.2), plus Φ=1.

Table 1a and Table 1b provide the ignition delay times, $t_{id,}$ predicted by the reference detailed GRI-Mech 3.0 mechanism as function of temperature, for P=1atm, and at Φ previously indicated (Tables 12a-12b and 23a-23b report data respectively at P=3atm and P=5atm).

Reactants Temperature, K	**Φ=0.3**	**Φ=0.5**	**Φ=0.7**	**Φ=0.9**	**Φ=1**
1000	0.608	0.772	0.982	1.03	1.04
1100	0.111	0.143	0.131	0.192	0.202
1200	0.0244	0.0314	0.0331	0.0424	0.044
1300	0.00649	0.00815	0.000967	0.011	0.0114
1400	0.00211	0.00247	0.00289	0.00323	0.00336
1500	0.000881	0.000915	0.00103	0.00112	0.00114
1600	0.000422	0.000398	0.000423	0.000439	0.000456
1700	0.000246	0.000197	0.000203	0.000203	0.000211
1800	0.000174	0.000108	0.000106	0.000107	0.000109
1900	0.000148	0.000067	0.0000638	0.0000627	0.0000628
2000	0.000139	0.0000398	0.0000381	0.0000375	0.0000377

Table 1. a Ignition Delay, s, P=1atm

Reactants Temperature, K	**Φ=1.1**	**Φ=1.3**	**Φ=1.5**	**Φ=1.7**	**Φ=1.9**
1000	1.15	1.2	1.22	1.43	1.53
1100	0.216	0.23	0.232	0.233	0.292
1200	0.0473	0.0522	0.0524	0.0523	0.0642
1300	0.0122	0.0134	0.0142	0.0155	0.0163
1400	0.00355	0.0039	0.00425	0.00445	0.00433
1500	0.00121	0.00127	0.00133	0.00143	0.00152
1600	0.00044	0.000492	0.000525	0.000529	0.000533
1700	0.000213	0.000221	0.00023	0.000236	0.000244
1800	0.000111	0.000112	0.000112	0.000116	0.00012
1900	0.000062	0.0000622	0.0000623	0.0000627	0.0000638
2000	0.0000374	0.0000376	0.0000384	0.0000385	0.0000392

Table 1. b Ignition Delay, s, P=1atm

From Tables 1a-1b, Tables 12a-12b and Tables 23a-23b it is possible to define a reactants temperature range where reactions might be completed, that is a range in which the Damkoehler number (residence time/chemical time) is less than 1. For example these tables indicate that ignition delay times vary between 8.43×10^{-6}s and 1.54s. Figure 1 reports the ignition delay (t_{id}), at Φ = 1, as function of reactants temperature and for the different reaction mechanisms.

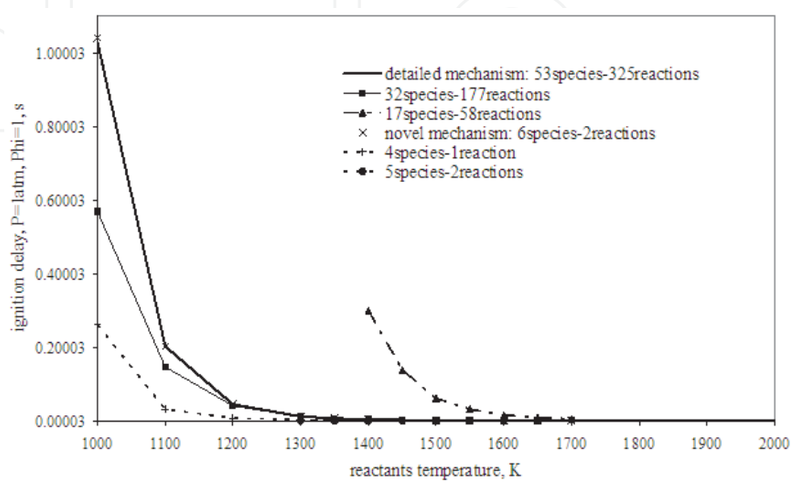


Fig. 1. Φ=1.0: t_{id} comparison

Tables 2 to 11 show the percent differences between the t_{id} predicted by GRI-Mech 3.0 and the reduced mechanisms tested (that is, GRI-Mech3.0 - Reduced Mechanism)/GRI-Mech3.0) at pressure equal to 1atm and for all the equivalence ratios mentioned above. Negative percentages mean that the reduced mechanism overpredicts the reference.
Blank spaces mean that no convergence or no ignition has been obtained at that temperature.
Tables, instead of figures, have been chosen for clarity (in some cases differences are too large).

	Mechanisms				
Reactants Temperature	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	42.93%		-4176.32%		
1100	25.86%		-2152.25%		
1200	10.25%		-1400.00%		
1300	0.62%		-1166.56%		
1400	-3.79%	-13075.36%	-1298.10%		
1500	0.00%	-6347.22%	-1534.51%		
1600	-3.79%	-3383.41%	-1817.06%		
1700	-6.50%	-1822.76%	-1900.00%		
1800	-9.77%	-974.71%	-1721.84%		
1900	-16.22%	-513.51%	-1352.70%		
2000	-34.53%	-308.63%	-1000.72%		

Table 2. Φ=0.3: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	45.34%		-576.17%		
1100	27.97%		-455.24%		
1200	12.74%		-355.41%		
1300	1.35%		-271.78%		
1400	-3.64%		-275.30%		
1500	-5.36%	-6468.31%	-331.69%		
1600	-6.53%	-3744.22%	-407.54%		
1700	-8.63%	-2331.47%	-488.83%		
1800	-8.33%	-1557.41%	-572.22%		
1900	-2.69%	-1050.75%	-614.93%		
2000	-7.79%	-847.24%	-736.68%		

Table 3. Φ=0.5: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	56.31%		-125.05%		
1100	6.87%		-206.11%		
1200	-0.30%		-145.92%		
1300	1.34%		-85.11%	84.59%	91.52%
1400	-4.50%		-72.66%	84.15%	91.28%
1500	-1.94%	-5919.42%	-90.29%	83.98%	91.21%
1600	-7.09%	-3611.58%	-134.75%	84.00%	91.61%
1700	-7.88%	-2303.94%	-181.28%	84.53%	93.89%
1800	-9.43%	-1616.98%	-233.96%		
1900	-7.05%	-1121.00%	-263.64%		
2000	-9.97%	-871.13%	-317.32%		

Table 4. Φ=0.7: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	49.13%		-18.45%		
1100	33.85%		-30.73%		
1200	12.03%		-28.07%		
1300	5.45%		-9.09%	84.82%	91.64%
1400	-5.88%	-9590.40%	-5.88%	84.43%	91.21%
1500	-5.36%	-5542.86%	-14.29%	83.13%	90.98%
1600	-10.48%	-3544.65%	-43.05%	82.44%	90.75%
1700	-12.32%	-2338.42%	-76.35%	82.32%	90.49%
1800	-13.08%	-1619.63%	-106.54%		
1900	-10.05%	-1161.56%	-129.67%		
2000	-12.00%	-908.00%	-162.93%		

Table 5. Φ=0.9: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	44.76%		-0.97%	74.66%	86.21%
1100	27.72%		0.00%	84.60%	90.54%
1200	9.09%		-5.00%	84.05%	91.36%
1300	1.75%		5.26%	84.74%	92.01%
1400	-2.72%		0.00%	84.88%	83.38%
1500	-1.40%	-8828.57%	3.57%	90.54%	84.35%
1600	-0.88%	-7087.50%	1.56%	89.84%	84.38%
1700	-0.53%	-5207.02%	-5.26%	82.98%	84.47%
1800	-0.19%	-4280.28%	-15.35%	85.21%	85.49%
1900	-0.17%	-3255.26%	-28.95%	82.46%	84.96%
2000	-0.28%	-2768.42%	-28.62%	83.55%	86.41%

Table 6. Φ=1.0: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	48.52%		29.30%	80.96%	
1100	29.63%		20.37%	85.28%	
1200	10.99%		15.01%	84.97%	
1300	0.00%		22.21%	84.75%	91.64%
1400	-6.76%	-8857.75%	26.76%	84.51%	91.15%
1500	-8.26%	-5197.52%	22.40%	82.98%	90.66%
1600	-18.18%	-3581.82%	-1.82%	80.41%	89.73%
1700	-12.21%	-2252.11%	-19.72%	81.22%	90.23%
1800	-9.91%	-1575.68%	-41.44%	81.89%	90.63%
1900	-12.68%	-1187.32%	-63.72%	82.66%	5.14%
2000	-13.37%	-926.74%	-86.36%	83.48%	91.28%

Table 7. Φ=1.1: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	50.56%		51.43%	75.24%	90.40%
1100	31.65%		44.73%	82.57%	90.84%
1200	11.69%		40.61%	84.54%	92.07%
1300	1.49%		43.81%	84.55%	91.72%
1400	-5.64%	-8156.41%	45.90%	84.38%	91.95%
1500	-11.81%	-5002.36%	41.65%	83.31%	90.24%
1600	-11.99%	-3213.01%	29.67%	80.67%	89.76%
1700	-13.12%	-2171.49%	11.31%	80.90%	90.41%
1800	-12.50%	-1578.57%	-7.14%	81.43%	90.00%
1900	-14.61%	-1203.37%	-25.52%	80.74%	89.70%
2000	-14.63%	-937.23%	-42.02%	81.73%	90.29%

Table 8. Φ=1.3: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	48.69%		58.28%	73.93%	90.00%
1100	21.98%		56.03%	82.03%	90.56%
1200	4.58%		51.53%	95.42%	92.02%
1300	-2.82%		53.87%	84.37%	91.62%
1400	-5.88%	-7547.06%	58.12%	83.72%	92.54%
1500	-13.53%	-4817.29%	53.61%	80.98%	89.92%
1600	-11.05%	-3023.81%	45.52%	80.19%	89.70%
1700	-13.04%	-2113.04%	30.87%	79.30%	90.35%
1800	-16.96%	-1596.43%	13.21%	80.63%	77.59%
1900	-17.98%	-1219.42%	-1.61%	81.86%	95.92%
2000	-14.84%	-931.25%	-12.50%	89.97%	93.46%

Table 9. Φ=1.5: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	49.30%		71.26%	77.62%	91.40%
1100	16.88%		60.69%	81.86%	90.43%
1200	-64.71%		31.58%	71.73%	84.33%
1300	-1.29%		63.48%	84.45%	91.68%
1400	-8.09%	-7270.79%	64.94%	83.96%	91.01%
1500	-12.59%	-4508.39%	63.08%	80.77%	89.86%
1600	-16.45%	-3019.09%	54.06%	78.64%	88.62%
1700	-14.83%	-2069.49%	42.37%	78.22%	88.98%
1800	-31.90%	-1555.17%	29.48%	79.05%	89.91%
1900	-20.41%	-1225.36%	15.15%	77.19%	87.93%
2000	-17.14%	-944.16%	5.45%	78.70%	88.83%

Table 10. Φ=1.7: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	52.22%		79.28%	78.95%	91.90%
1100	30.82%		75.45%	82.36%	92.40%
1200	11.06%		70.25%	84.27%	91.98%
1300	-3.07%		69.14%	83.99%	91.60%
1400	-18.24%	-7544.34%	68.13%	81.27%	90.12%
1500	-12.50%	-4268.42%	69.01%	80.53%	89.74%
1600	-17.82%	-3014.45%	60.23%	77.11%	88.16%
1700	-15.57%	-2002.46%	52.87%	77.17%	87.70%
1800	-17.50%	-1516.67%	40.92%	76.92%	90.00%
1900	-21.79%	-1216.61%	27.74%	75.71%	87.21%
2000	-18.37%	-938.27%	19.64%	77.32%	88.14%

Table 11. Φ=1.9: t_{id} % differences between reduced and reference mechanisms

Tables 2-11 above (P=1atm) show that:

- at Φ=0.3 and Φ=0.5 the Westbrook and Dryer mechanisms do not predict ignition at any temperature and ignite in a narrow T range at Φ=0.7 and Φ=0.9. This is worthily since many researchers use this mechanism out of context, e.g., to predict properties of *non-premixed* flames.
- when the Westbrook and Dryer mechanisms ignite, the single step behaves better than the 2-step. Percentage differences are almost constant, that is 80% for the mechanism with 1 reaction and 90% for the mechanism with 2 reactions;
- the Kee mechanism (17 species and 58 reactions) starts predicting ignition only at temperatures > 1400K and consistently overpredicts reference values (differences are 13000% at low Φ);
- even though differences are significant in some T range, the Minotti (6 species and 2 reactions) predicts the 'best' t_{id} at every equivalence ratio except Φ=0.7;
- Minotti predicts realistically t_{id} at Φ=1; in particular from 1000K to 1700K the difference is < 5%, sometimes even <1% and better than GRIMech 12 predictions which adopts 32 species and 177 reactions;
- the GRI-Mech 12 (32 species and 177 reactions) usually fits the reference values better than the other mechanisms;

Ignition delay times at P=3atm and P=5atm are also compared and provided.
Here tables 12a-12b and 13a-13b, report the ignition delay times of the GRIMech3.0 detailed mechanism at P=3atm and P=5atm.

Reactants Temperature, K	**Φ=0.3**	**Φ=0.5**	**Φ=0.7**	**Φ=0.9**	**Φ=1**
1000	0.206	0.238	0.273	0.302	0.302
1100	0.0385	0.0474	0.0562	0.0632	0.0641
1200	0.00957	0.0114	0.0133	0.0152	0.0152
1300	0.00266	0.00324	0.00383	0.00433	0.00438
1400	0.000878	0.00104	0.00122	0.00133	0.00133
1500	0.000341	0.000385	0.000433	0.000479	0.000481
1600	0.000156	0.000163	0.000174	0.000186	0.000187
1700	0.0000822	0.0000767	0.0000808	0.0000836	0.0000838
1800	0.0000503	0.0000404	0.0000408	0.0000416	0.0000417
1900	0.0000356	0.0000234	0.0000227	0.0000228	0.0000228
2000	0.0000291	0.0000144	0.0000136	0.0000134	0.0000134

Table 12. a Ignition Delay, s, P=3atm

Reactants Temperature, K	**Φ=1.1**	**Φ=1.3**	**Φ=1.5**	**Φ=1.7**	**Φ=1.9**
1000	0.332	0.225	0.401	0.432	0.462
1100	0.071	0.0641	0.0826	0.0902	0.0962
1200	0.0172	0.0191	0.0202	0.0221	0.0233
1300	0.00426	0.00591	0.00527	0.00622	0.00631
1400	0.00151	0.00191	0.00172	0.00185	0.00201
1500	0.000521	0.00066	0.000601	0.000636	0.000631
1600	0.000201	0.000248	0.000222	0.000235	0.000248
1700	0.0000874	0.000103	0.0000924	0.0000972	0.000102
1800	0.0000427	0.000051	0.0000451	0.0000465	0.0000479
1900	0.0000231	0.0000272	0.0000239	0.0000244	0.0000251
2000	0.0000135	0.0000159	0.0000139	0.0000141	0.0000143

Table 12. b Ignition Delay, s, P=3atm

Reactants Temperature, K	Φ=0.3	Φ=0.5	Φ=0.7	Φ=0.9	Φ=1
1000	0.125	0.134	0.153	0.17	0.172
1100	0.0234	0.0274	0.0322	0.0362	0.0382
1200	0.00577	0.00682	0.00827	0.00923	0.00982
1300	0.0017	0.00204	0.00242	0.00272	0.00282
1400	0.000578	0.000685	0.000738	0.000886	0.000921
1500	0.000228	0.000255	0.000285	0.000316	0.000331
1600	0.000101	0.000106	0.000114	0.000123	0.000131
1700	0.0000519	0.0000504	0.0000529	0.0000555	0.0000571
1800	0.0000303	0.0000262	0.0000264	0.0000272	0.0000275
1900	0.0000202	0.0000147	0.0000145	0.0000146	0.0000147
2000	0.0000154	0.00000893	0.00000868	0.00000843	0.00000861

Table 13. a Ignition Delay, s, P=5atm

Reactants Temperature, K	Φ=1.1	Φ=1.3	Φ=1.5	Φ=1.7	Φ=1.9
1000	0.182	0.202	0.213	0.233	0.248
1100	0.0402	0.044	0.0472	0.0512	0.0543
1200	0.0102	0.0112	0.0122	0.0132	0.0141
1300	0.00301	0.00328	0.00352	0.00381	0.00402
1400	0.000975	0.00102	0.00112	0.00122	0.00128
1500	0.000342	0.000371	0.000391	0.000422	0.00043
1600	0.000132	0.000142	0.000131	0.00016	0.000166
1700	0.0000582	0.0000612	0.0000623	0.0000665	0.000068
1800	0.000028	0.0000289	0.0000298	0.0000308	0.0000318
1900	0.0000149	0.0000151	0.0000154	0.0000159	0.0000163
2000	0.00000845	0.00000872	0.00000877	0.00000902	0.00000916

Table 13. b Ignition Delay, s, P=5atm

Tables A1-A10 and A11-A20 (in the appendix) report, respectively, the percentage differences at P=3atm and at P=5atm.
Tables A1-A20 show that reaction mechanisms worse their accuracy increasing the operating pressure to P=3atm and P=5 atm, in fact:

- the 1-step and 2-step Westbrook and Dryer mechanisms start igniting only at Φ= 1.0 and Φ=1.1, respectively, both for P=3atm and P=5atm (at P=1atm ignition occurs for Φ>0.7).
- the Kee mechanism predicts ignition only at T > 1500K, both at P=3atm and P=5atm, (at P=1atm the minimum temperature is 1400K), and it consistently overpredicts reference values;
- the Minotti 'ignites' at all Φ, both for P=3atm and P=5atm, behaves worse than at 1atm;
- the single-step Westbrook and Dryer mechanism when it ignites, behaves better than the two-step and the Minotti mechanism;
- the GRI-Mech 12 usually fits the reference values better than the other mechanisms.

5. Comparison – equilibrium temperatures

A parallel comparison was carried out for the equilibrium temperatures predictions.
Table 14a-14b report the temperature predicted by the GRI-Mech 3.0, when equilibrium is reached, as a function of **Φ** and reactants temperature, at P=1atm.

Figures 2 to 11 report equilibrium temperature at P= 1, from Φ=0.3 to Φ=1.9 as function of reactants temperature.
Simulations were carried out up to one hundred times the ignition delay.

Reactants Temperature, K	Φ=0.3	Φ=0.5	Φ=0.7	Φ=0.9	Φ=1
1000	1682	2043	2325	2497	2517
1100	1774	2123	2387	2541	2560
1200	1866	2201	2445	2584	2601
1300	1956	2276	2499	2626	2641
1400	2046	2347	2551	2665	2680
1500	2135	2417	2602	2704	2717
1600	2218	2482	2650	2742	2753
1700	2298	2542	2689	2777	2789
1800	2373	2591	2730	2812	2823
1900	2445	2643	2770	2845	2856
2000	2507	2692	2808	2878	2888

Table 14. a Temperature at Steady State, K, P=1atm

Reactants Temperature, K	Φ=1.1	Φ=1.3	Φ=1.5	Φ=1.7	Φ=1.9
1000	2559	2516	2516	2287	2165
1100	2600	2570	2570	2364	2247
1200	2640	2621	2621	2438	2327
1300	2499	2626	2602	2508	2405
1400	2551	2665	2658	2574	2479
1500	2602	2704	2709	2636	2549
1600	2650	2742	2756	2693	2614
1700	2689	2777	2799	2745	2675
1800	2853	2861	2861	2793	2731
1900	2885	2894	2877	2838	2783
2000	2915	2926	2913	2879	2831

Table 14. b Temperature at Steady State, K, P=1atm

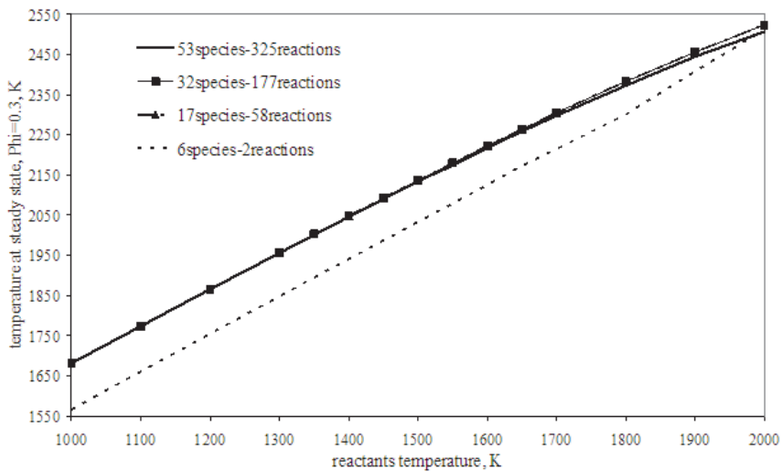


Fig. 2. Φ=0.3, P=1atm, temperature

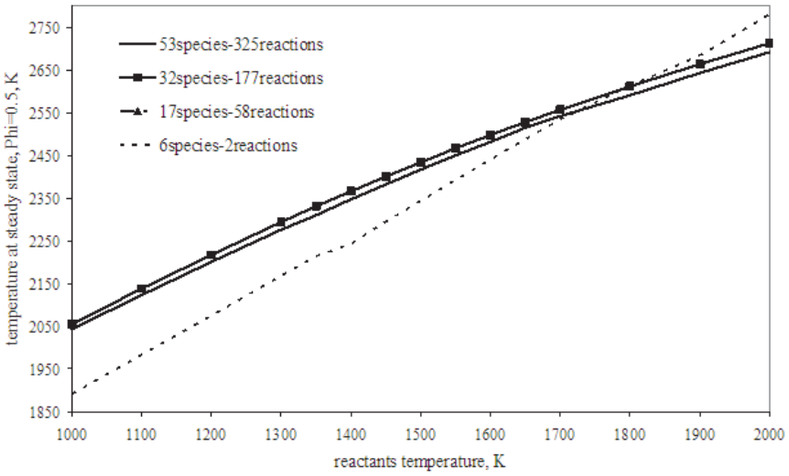


Fig. 3. Φ=0.5, P=1atm, temperature

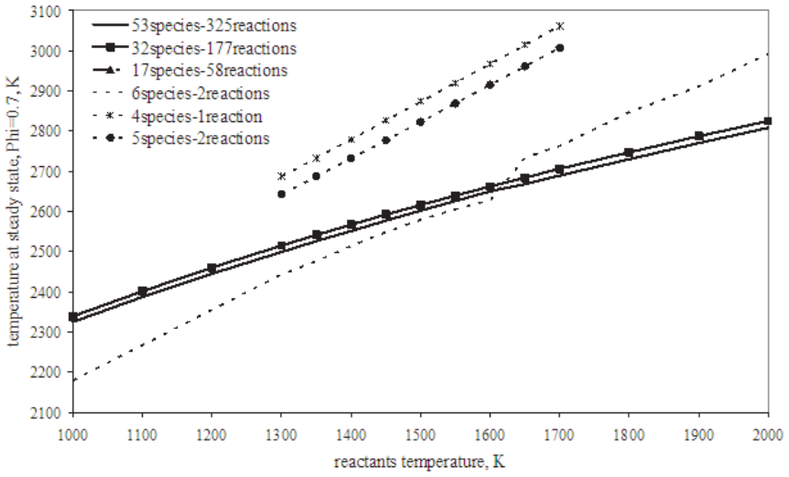


Fig. 4. Φ=0.7, P=1atm, temperature

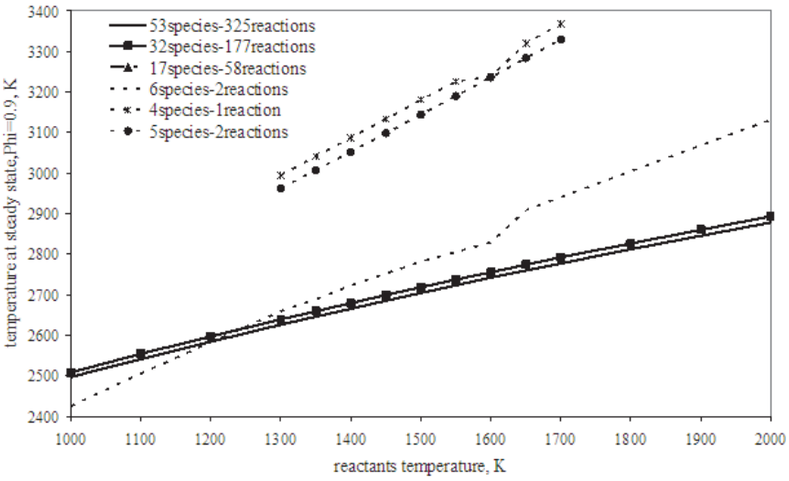


Fig. 5. Φ=0.9, P=1atm, temperature

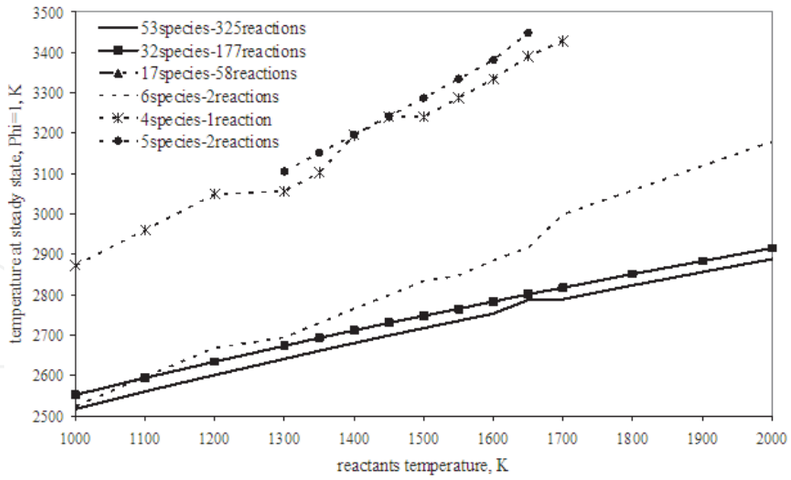


Fig. 6. Φ=1.0, P=1atm, temperature

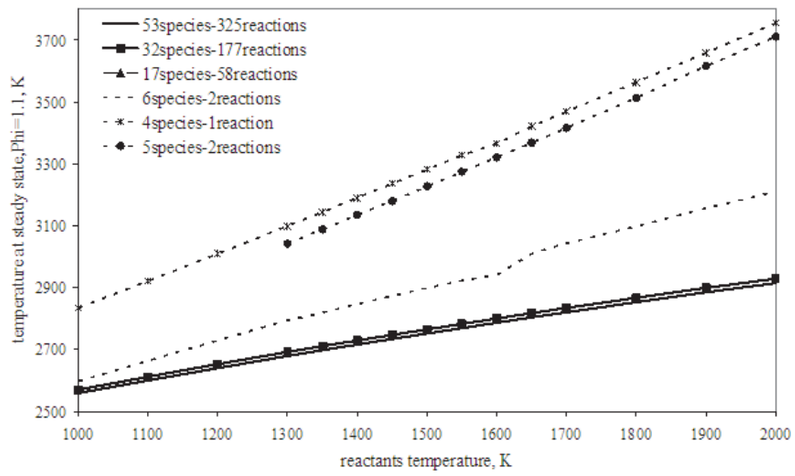


Fig. 7. Φ=1.1, P=1atm, temperature

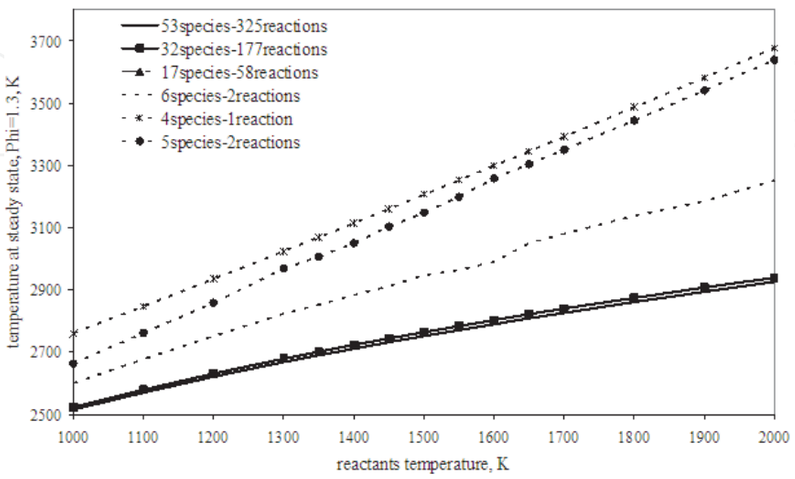


Fig. 8. Φ=1.3, P=1atm, temperature

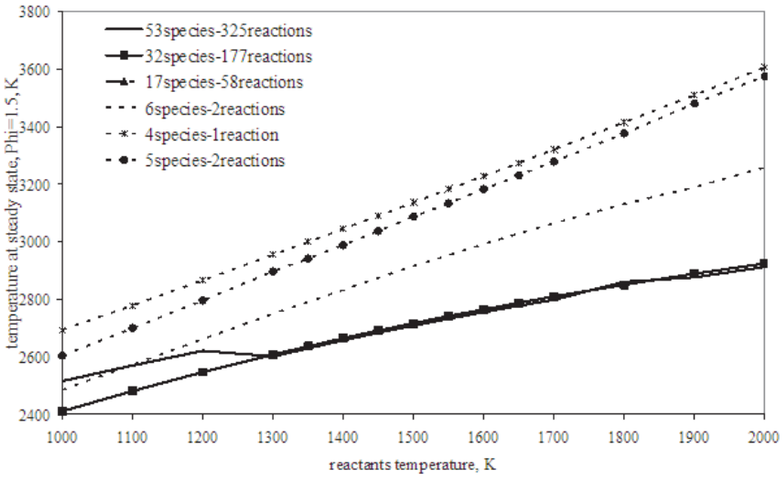


Fig. 9. Φ=1.5, P=1atm, temperature

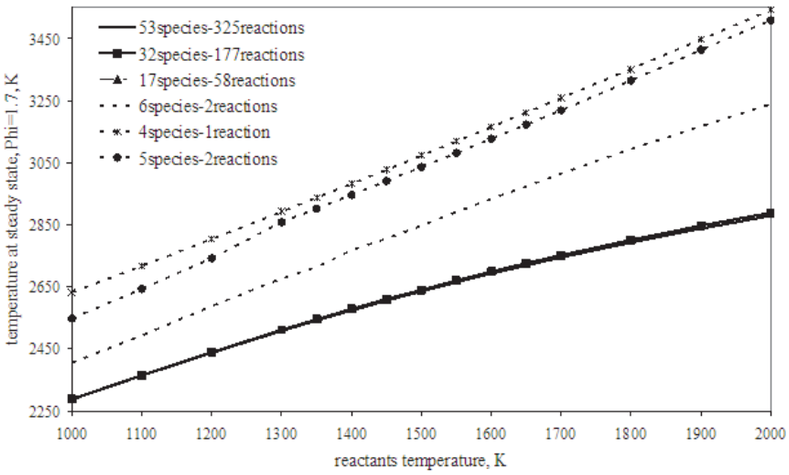


Fig. 10. Φ=1.7, P=1atm, temperature

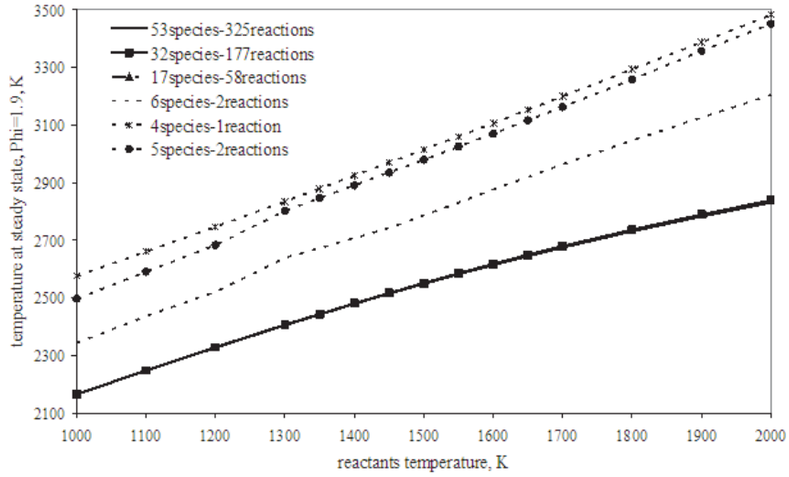


Fig. 11. Φ=1.9, P=1atm, temperature

Above results indicate that:

- Minotti predicted temperatures are always much closer to reference than using the two Westbrook and Dryer mechanisms (when they ignite);
- Minotti mechanism is much more accurate than the other semiglobal W&D mechanisms; accuracy (in percentage difference) is at least of the double, but for some temperature and equivalence ration ranges it reaches grade of accuracy of 4 times better;
- unlike the ignition delay times, mechanisms with large number of reactions and species predict temperatures, *when they ignite*, with always higher accuracy than reduced mechanisms (those predicted with the Kee mechanism, differently from the ignition delay, are close to reference);
- the GRI-Mech 12 usually fits the reference values better than the other mechanisms.

Tables 15a-15b and 16a-16b provide the Temperature at Steady State at pressures equal to 3 and 5atm predicted by the GRIMech3.0 (detailed mechanism). Figures A1-A10 and A11-A20 (in the Appendix) report equilibrium temperature, respectively, at P=3atm and at P=5atm, from Φ=0.3 to Φ=1.9 as function of reactants temperature.

Reactants Temperature, K	**Φ=0.3**	**Φ=0.5**	**Φ=0.7**	**Φ=0.9**	**Φ=1**
1000	1682	2047	2346	2543	2549
1100	1774	2130	2413	2593	2598
1200	1866	2210	2477	2641	2646
1300	1958	2289	2538	2687	2692
1400	2051	2366	2596	2732	2736
1500	2140	2438	2651	2775	2779
1600	2230	2511	2703	2817	2821
1700	2315	2578	2753	2858	2861
1800	2397	2651	2800	2898	2901
1900	2475	2705	2847	2936	2939
2000	2545	2756	2890	2973	2976

Table 15. a Temperature at Steady State, K, P=3atm

Reactants Temperature, K	**Φ=1.1**	**Φ=1.3**	**Φ=1.5**	**Φ=1.7**	**Φ=1.9**
1000	2611	2554	2426	2296	2170
1100	2659	2619	2501	2377	2255
1200	2704	2680	2573	2457	2339
1300	2748	2737	2642	2534	2422
1400	2790	2790	2706	2608	2502
1500	2831	2839	2766	2678	2580
1600	2870	2885	2822	2744	2654
1700	2909	2928	2873	2806	2723
1800	2946	2969	2922	2863	2789
1900	2982	3008	2967	2916	2850
2000	3017	3045	3009	2966	2907

Table 15. b Temperature at Steady State, K, P=3atm

Reactants Temperature, K	Φ=0.3	Φ=0.5	Φ=0.7	Φ=0.9	Φ=1
1000	1682	2048	2353	2562	2618
1100	1774	2131	2423	2615	2666
1200	1867	2214	2490	2665	2713
1300	1960	2294	2554	2714	2758
1400	2052	2372	2615	2761	2802
1500	2144	2447	2673	2807	2845
1600	2234	2521	2728	2851	2887
1700	2321	2590	2780	2894	2928
1800	2404	2655	2831	2936	2968
1900	2483	2722	2878	2977	3007
2000	2561	2778	2924	3016	3045

Table 16. a Temperature at Steady State, K, P=5atm

Reactants Temperature, K	Φ=1.1	Φ=1.3	Φ=1.5	Φ=1.7	Φ=1.9
1000	2634	2560	2431	2299	2171
1100	2684	2626	2509	2380	2257
1200	2732	2690	2584	2463	2343
1300	2778	2749	2656	2543	2427
1400	2823	2804	2725	2620	2511
1500	2866	2855	2789	2649	2591
1600	2908	2904	2849	2764	2668
1700	2949	2950	2905	2830	2742
1800	2988	2993	2957	2892	2812
1900	3026	3034	3006	2949	2877
2000	3064	3074	3051	3003	2938

Table 16. b Temperature at Steady State, K, P=5atm

Figures A1-A20 (in the appendix) show that all reaction mechanisms, but the Minotti one, worse their accuracy increasing the operating pressure to P=3atm and P=5 atm, in fact:

- the 1-step and 2-step Westbrook and Dryer mechanisms do not predict ignition for wide ranges of equivalence ratio both for P=3atm and P=5atm (at P=1atm ignition occurs for Φ>0.7); moreover the 2-step mechanism is slightly more accurate than the 1-step mechanism;
- the Minotti 'ignites' at all Φ, and it holds its overall level of accuracy and it behaves better than at P=1atm for some ranges of temperature and equivalence ratio;
- Minotti mechanism is much more accurate than the other semiglobal W&D mechanisms; accuracy (in percentage difference) is at least of the double, but, for some temperature and equivalence ratio ranges, it reaches grade of accuracy of 100 times better.
- the Kee mechanism predicts ignition only at T > 1500K, both at P=3atm and P=5atm, (at P=1atm the minimum temperature is 1400K), and it predicts values with high level of accuracy;
- the GRI-Mech 12 usually fits the reference values better than the other mechanisms.

6. Conclusions

Current studies on space missions and on micro-combustion, also for Micro-Rockets applications, gave the cue for the present work.
This chapter focuses its attention on some of the most important points concerning with reaction mechanisms and, at same time, five mechanisms are presented, analysed and compared; they deal with hydrocarbon oxidation, in particular methane. Comparison is carried out for a wide range of equivalence ratios ($0.3 \leq \Phi \leq 1.9$), temperatures (1000K-2000K) and pressure ($1 \leq P\ [atm] \leq 5$), adopting as benchmark the detailed GRIMech3.0 reference mechanism, which adopts 55 species and 325 reactions.
This study is important because analyses the mechanisms effectiveness in predicting ignition in good agreement with detailed kinetics calculations with low temperature and low pressures ignition ranges.
These ranges are typical of non-adiabatic combustion and, unfortunately, reduced mechanisms found in literature often fail to predict realistic delay times and equilibrium flame temperatures under these conditions but are usually adopted without a previous validity study. In applications where the flame temperature is lower or much lower than adiabatic, realism and accuracy are indeed critical.
Some general results may be summarised.
Among the semiglobal mechanisms, the Minotti 2-step reduced mechanism is well suited for low temperature flames, that is, in devices where heat losses, e.g., through non-adiabatic walls, are not negligible. Results are in some cases surprising, showing this mechanism predicts, in some ranges, ignition delay times and equilibrium temperatures better than other reduced and even detailed mechanisms, showing also that it 'ignites' at all P and Φ.
Thus it is not always true that including larger numbers of species and reactions predict ignition delays better, in fact there are wide ranges of T and Φ in which the Kee mechanism (17 species and 58 reactions) does not ignite and/or is less accurate than other simplified mechanisms. The Westbrook and Dryer mechanisms ignite only at particular equivalence ratios and at particular reactants temperature.
As for the effect of pressure, at 1atm the Minotti mechanism predicts ignition delays times always more accurately than the other reduced mechanisms, except at $\Phi=0.7$ and for $1500<T\ [K]<1700$, where the two Westbrook and Dryer mechanisms behave better. At 3 and 5 atm the behavior is in general the same.
The comparison among predicted equilibrium temperature has shown that mechanisms with high number of species, predict final (stationary) temperatures, when they ignite, better than mechanism with a lower number of species, as it is expected since simpler mechanism cannot include radicals. Comparisons are then meaningful only between mechanisms with similar numbers of species and reactions.
This said, Minotti one is always much more accurate than the two Westbrook and Dryer mechanisms.
To conclude the Minotti mechanism is appropriate for preliminary combustion studies in all the devices that operate at low temperature and pressure, as it combines high accuracy and reliability with ease of implementation and a modest computational effort.

7. Appendix

Ignition delay, P=3atm and P=5atm, comparison

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	29.61%		-2919.42%		
1100	7.01%		-858.44%		
1200	0.00%		-377.53%		
1300	-10.90%		-217.29%		
1400	-11.50%		-172.21%		
1500	-9.97%	-6996.77%	-190.91%		
1600	-8.33%	-3592.31%	-237.82%		
1700	-8.03%	-2004.62%	-284.43%		
1800	-9.34%	-1237.97%	-303.58%		
1900	-12.08%	-686.52%	-287.64%		
2000	-17.18%	-405.15%	-233.68%		

Table A1. P=3atm, Φ=0.3: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	31.51%		-144.54%		
1100	10.97%		-71.31%		
1200	-7.02%		-34.21%		
1300	-12.04%		-1.85%		
1400	-11.54%		18.46%		
1500	-12.47%	-6731.17%	24.16%		
1600	-7.98%	-3703.68%	17.18%		
1700	-9.13%	-2272.88%	1.43%		
1800	-8.91%	-1503.96%	-15.59%		
1900	-8.12%	-1053.85%	-31.20%		
2000	-7.64%	-781.94%	-46.53%		

Table A2. P=3atm, Φ=0.5: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	52.75%		31.14%		
1100	23.67%		37.54%		
1200	-6.02%		45.26%		
1300	-12.53%		50.39%		
1400	-14.75%		59.26%		
1500	-13.86%	-6251.04%	62.36%		
1600	-11.49%	-3624.14%	59.66%		
1700	-6.68%	-2226.73%	53.47%		
1800	-10.78%	-1529.90%	43.87%		
1900	-11.45%	-1120.26%	34.36%		
2000	-11.76%	-848.53%	11.76%		

Table A3. P=3atm, Φ=0.7: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	58.28%		69.83%		
1100	17.25%		68.20%		
1200	0.00%		71.91%		
1300	-11.55%		71.36%		
1400	-15.04%		74.59%		
1500	-15.24%	-5829.02%	76.62%		
1600	-14.52%	-3491.40%	75.32%		
1700	-11.48%	-2220.57%	71.53%		
1800	-12.98%	-1544.23%	65.63%		
1900	-13.16%	-1145.61%	59.34%		
2000	-13.43%	-892.54%	52.84%		

Table A4. P=3atm, Φ=0.9: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	36.42%		90.66%		
1100	15.60%		67.86%		
1200	0.00%		72.17%		
1300	-12.10%		71.92%		
1400	-19.55%		73.91%		
1500	-14.76%	-5804.37%	77.13%		
1600	-13.90%	-3477.54%	75.83%		
1700	-11.34%	-2215.04%	72.08%		
1800	-12.95%	-1542.69%	66.19%		
1900	-13.16%	-1145.61%	60.04%		
2000	-13.43%	-892.54%	53.66%		

Table A5. P=3atm, Φ=1.0: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	36.14%		81.72%	15.66%	
1100	26.34%		81.55%	55.21%	83.10%
1200	0.00%		81.57%	58.66%	81.57%
1300	-22.54%		78.36%	72.07%	78.64%
1400	-13.91%		84.24%	63.58%	81.13%
1500	-17.85%	-5466.22%	88.96%	59.50%	79.08%
1600	-12.94%	-3302.99%	84.38%	57.11%	79.55%
1700	-14.42%	-2165.45%	80.78%	54.12%	76.77%
1800	-14.75%	-1527.63%	76.11%	52.93%	75.88%
1900	-14.29%	-1151.08%	71.56%	53.25%	76.36%
2000	-14.07%	-900.00%	66.89%	54.22%	77.04%

Table A6. P=3atm, Φ=1.1: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	37.85%		88.65%	16.85%	58.29%
1100	11.59%		86.07%	43.03%	70.90%
1200	0.00%		88.59%	57.75%	78.59%
1300	-13.00%		86.25%	60.99%	80.69%
1400	-17.90%		86.42%	62.41%	80.86%
1500	-17.65%	-5176.29%	87.65%	58.65%	79.14%
1600	-16.98%	-3187.74%	87.26%	55.14%	77.36%
1700	-12.94%	-2114.91%	85.75%	53.73%	75.33%
1800	-16.17%	-1517.31%	82.07%	49.43%	74.26%
1900	-16.24%	-1156.41%	78.46%	48.72%	74.02%
2000	-16.06%	-907.30%	75.04%	49.85%	75.33%

Table A7. P=3atm, Φ=1.3: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	43.64%		92.19%	17.46%	59.85%
1100	24.33%		90.24%	49.52%	73.61%
1200	0.00%		89.46%	58.12%	79.41%
1300	-18.22%		88.35%	57.87%	78.94%
1400	-17.44%		91.92%	59.77%	81.69%
1500	-18.80%	-4908.32%	90.25%	64.23%	80.70%
1600	-18.47%	-3093.69%	89.95%	53.15%	77.07%
1700	-20.13%	-2118.61%	88.10%	48.48%	76.84%
1800	-17.74%	-1496.45%	85.83%	46.12%	72.73%
1900	-17.57%	-1151.05%	82.89%	45.19%	72.43%
2000	-17.27%	-907.19%	80.14%	45.97%	72.88%

Table A8. P=3atm, Φ=1.5: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	41.67%		94.93%	18.75%	60.19%
1100	19.84%		97.02%	53.55%	75.61%
1200	4.07%		94.48%	58.69%	81.09%
1300	-9.49%		91.72%	65.11%	80.71%
1400	-19.46%		93.19%	61.41%	82.49%
1500	-19.50%	-4711.32%	91.71%	64.47%	78.30%
1600	-19.57%	-2959.57%	91.70%	51.91%	76.21%
1700	-20.37%	-2039.92%	90.77%	47.12%	75.93%
1800	-18.92%	-1469.89%	88.39%	43.01%	71.40%
1900	-19.26%	-1141.80%	85.94%	41.39%	70.66%
2000	-18.44%	-914.18%	83.48%	41.84%	70.92%

Table A9. P=3atm, Φ=1.7: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	41.13%		95.32%	17.53%	59.31%
1100	19.85%		94.66%	46.47%	72.87%
1200	0.43%		94.81%	56.65%	78.11%
1300	-14.90%		93.34%	58.80%	79.40%
1400	-14.93%	-8009.45%	93.83%	60.05%	79.90%
1500	-28.68%	-4812.84%	95.28%	53.09%	76.55%
1600	-19.76%	-2839.52%	93.35%	50.81%	75.56%
1700	-19.61%	-1958.82%	93.17%	45.39%	73.53%
1800	-20.25%	-1444.89%	90.21%	40.29%	70.15%
1900	-19.92%	-1127.09%	88.09%	38.25%	69.28%
2000	-20.28%	-913.99%	85.87%	37.83%	69.37%

Table A10. P=3atm, Φ=1.9: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	23.60%		-3020.00%		
1100	-0.43%		-652.14%		
1200	-13.69%		-225.82%		
1300	-20.00%		-87.65%		
1400	-17.47%		-39.45%		
1500	-13.16%	-7838.60%	-32.02%		
1600	-9.90%	-3919.80%	-49.50%		
1700	-8.67%	-2115.80%	-71.10%		
1800	-9.24%	-1236.63%	-87.46%		
1900	-10.89%	-746.53%	-89.60%		
2000	-13.64%	-452.60%	-75.32%		

Table A11. P=5atm, Φ=0.3: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	23.13%		-80.60%		
1100	0.73%		-9.85%		
1200	-15.98%		20.53%		
1300	-19.12%		40.20%		
1400	-20.15%		55.47%		
1500	-16.86%	-7664.71%	62.31%		
1600	-16.04%	-4098.11%	61.60%		
1700	-10.71%	-2360.32%	57.14%		
1800	-9.54%	-1518.32%	50.00%		
1900	-10.88%	-1063.27%	41.63%		
2000	-9.07%	-780.18%	34.15%		

Table A12. P=5atm, Φ=0.5: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	26.80%		60.13%		
1100	0.31%		63.35%		
1200	-10.16%		72.91%		
1300	-16.94%		73.97%		
1400	-30.08%		79.95%		
1500	-20.00%	-7198.25%	85.79%		
1600	-17.54%	-4022.81%	80.70%		
1700	-13.42%	-2357.47%	79.21%		
1800	-12.88%	-1574.24%	75.49%		
1900	-12.41%	-1127.59%	71.24%		
2000	-9.79%	-836.64%	67.28%		

Table A13. P=5atm, Φ=0.7: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	29.65%		82.33%		
1100	8.29%		83.12%		
1200	-10.51%		86.89%		
1300	-18.38%		84.60%		
1400	-16.25%		86.00%		
1500	-20.89%	-6703.80%	87.85%		
1600	-17.89%	-3859.35%	87.97%		
1700	-15.68%	-2332.43%	87.19%		
1800	-14.34%	-1576.47%	85.00%		
1900	-14.38%	-1153.42%	82.19%		
2000	-15.90%	-892.88%	79.12%		

Table A14. P=5atm, Φ=0.9: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	29.07%		86.34%		
1100	8.12%		86.52%		
1200	-3.87%		86.66%		
1300	-20.92%		87.16%	37.23%	
1400	-21.61%		88.27%	44.63%	
1500	-21.45%	-6486.10%	89.73%	39.58%	
1600	-16.03%	-3678.63%	90.31%		
1700	-16.29%	-2299.30%	89.47%	33.45%	
1800	-16.00%	-1580.00%	87.60%	30.55%	
1900	-15.65%	-1158.50%	85.24%	30.61%	
2000	-14.63%	-884.90%	82.93%		

Table A15. P=5atm, Φ=1.0: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	32.97%		93.46%	-53.85%	27.47%
1100	9.95%		89.85%	5.22%	52.74%
1200	-9.80%		88.92%	30.29%	68.92%
1300	-16.94%		91.33%	38.21%	69.83%
1400	-21.03%		95.11%	43.59%	73.95%
1500	-23.10%	-6332.75%	90.99%	38.30%	69.88%
1600	-21.97%	-3695.45%	91.21%	34.70%	69.09%
1700	-10.48%	-2288.32%	91.07%	31.10%	65.46%
1800	-16.79%	-1571.43%	89.57%	28.21%	63.93%
1900	4.03%	-1155.03%	87.65%	27.52%	64.23%
2000	-17.87%	-915.38%	85.09%	26.86%	62.72%

Table A16. P=5atm, Φ=1.1: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	34.65%		93.37%	-51.49%	25.25%
1100	11.14%		92.95%	4.55%	51.82%
1200	-8.04%		92.58%	27.95%	63.84%
1300	-18.60%		92.50%	37.80%	69.21%
1400	-28.43%		92.53%	40.29%	69.71%
1500	-14.56%	-5964.69%	93.34%	37.47%	69.27%
1600	8.45%	-3505.63%	93.66%	33.03%	67.46%
1700	-17.65%	-2220.26%	93.28%	31.05%	63.89%
1800	-17.99%	-1553.98%	92.18%	22.49%	61.59%
1900	-17.88%	-1164.90%	90.40%	20.53%	60.40%
2000	-16.97%	-905.73%	89.12%	21.22%	62.04%

Table A17. P=5atm, Φ=1.3: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	33.33%		95.12%	-55.40%	24.41%
1100	10.81%		95.49%	4.24%	53.18%
1200	-6.56%		97.86%	30.66%	65.98%
1300	-19.32%		94.18%	36.93%	68.18%
1400	-25.89%		97.54%	38.21%	71.96%
1500	-25.58%	-5731.20%	94.42%	35.29%	68.29%
1600	-39.69%	-3884.73%	96.45%	20.61%	61.37%
1700	-23.43%	-2227.45%	94.56%	23.92%	61.48%
1800	-19.80%	-1537.58%	93.83%	18.46%	59.40%
1900	-19.48%	-1166.23%	92.47%	14.94%	58.12%
2000	-18.59%	-920.52%	91.61%	14.37%	58.15%

Table A18. P=5atm, Φ=1.5: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	34.76%		96.42%	-50.64%	90.60%
1100	12.30%		96.11%	4.30%	52.93%
1200	0.00%		95.83%	30.83%	68.33%
1300	-17.59%		95.54%	36.75%	68.77%
1400	-23.77%		95.48%	41.48%	74.02%
1500	-24.41%	-5397.63%	95.64%	46.45%	68.25%
1600	-21.25%	-3218.75%	95.80%	29.38%	66.06%
1700	-21.65%	-2110.53%	95.58%	22.71%	60.90%
1800	-21.10%	-1510.39%	95.00%	13.96%	57.47%
1900	-20.13%	-1151.57%	93.91%	10.06%	55.66%
2000	-19.73%	-911.09%	93.28%	9.09%	55.21%

Table A19. P=5atm, Φ=1.7: t_{id} % differences between reduced and reference mechanisms

Reactants Temperature	*Mechanisms*				
	32species 177reactions	17species 58reactions	6species 2reactions	4species 1reaction	5species 2reactions
1000	34.68%		98.90%	-53.63%	26.61%
1100	13.08%		97.77%	5.16%	53.22%
1200	-0.71%		98.01%	28.37%	64.18%
1300	-17.91%		96.99%	35.32%	68.66%
1400	-25.78%	-9821.88%	97.76%	37.27%	69.06%
1500	-30.23%	-5365.12%	96.98%	32.56%	66.28%
1600	-24.70%	-3146.99%	97.99%	26.51%	63.73%
1700	-25.44%	-2105.88%	96.16%	18.09%	58.82%
1800	-22.64%	-1484.91%	95.75%	10.06%	55.66%
1900	-22.09%	-1139.26%	95.11%	4.91%	53.68%
2000	-21.18%	-913.10%	94.26%	2.95%	53.06%

Table A20. P=5atm, Φ=1.9: t_{id} % differences between reduced and reference mechanisms

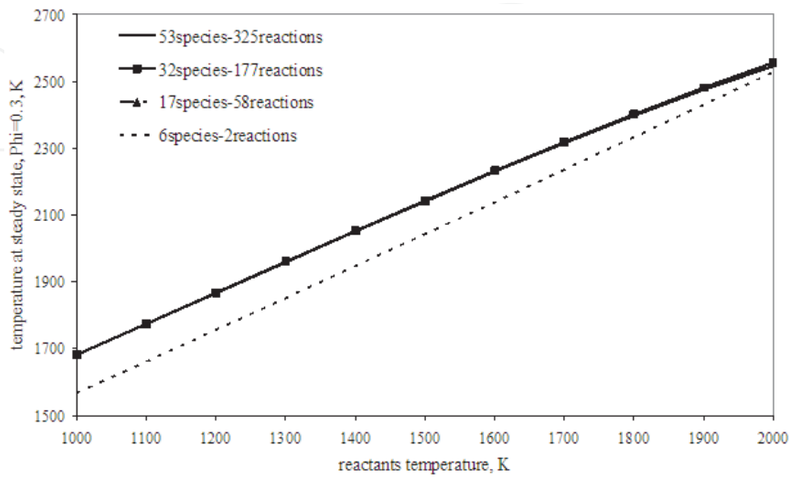


Fig. A1. Φ=0.3, P=3atm, temperature

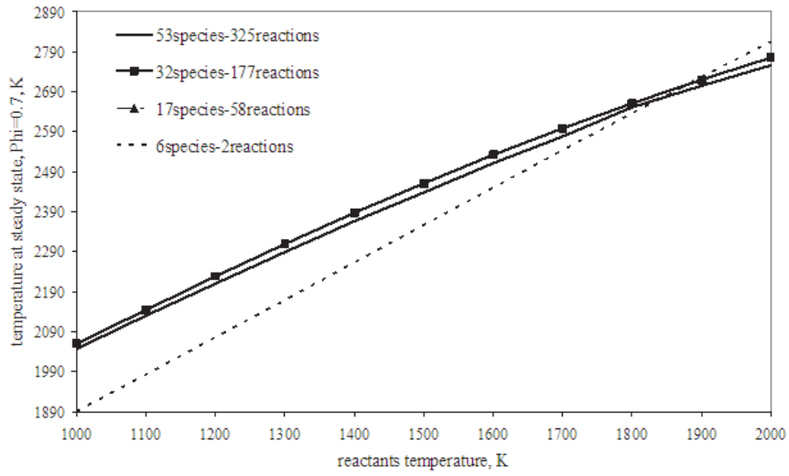


Fig. A2. Φ=0.5, P=3atm, temperature

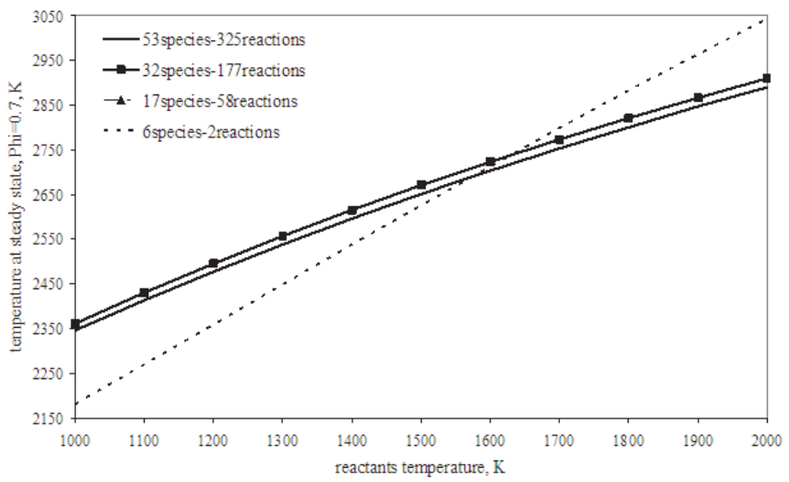


Fig. A3. Φ=0.7, P=3atm, temperature

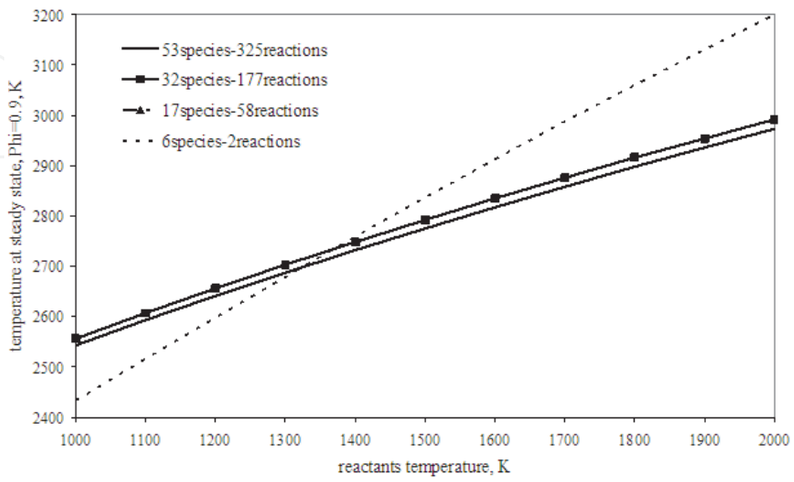


Fig. A4. Φ=0.9, P=3atm, temperature

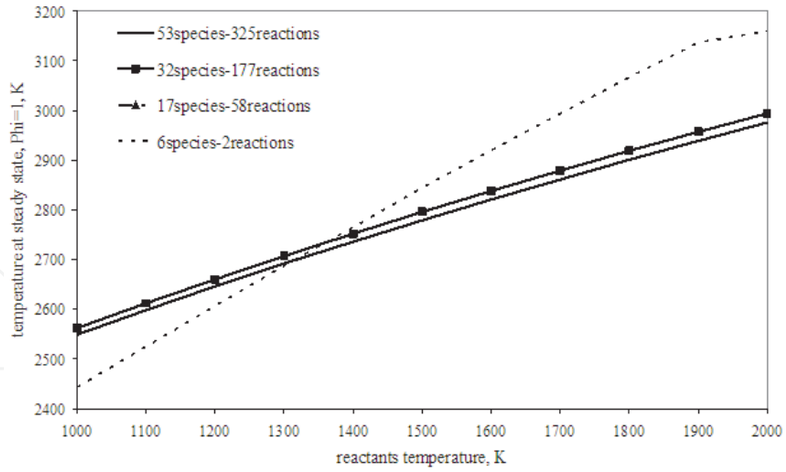


Fig. A5. Φ=1, P=3atm, temperature

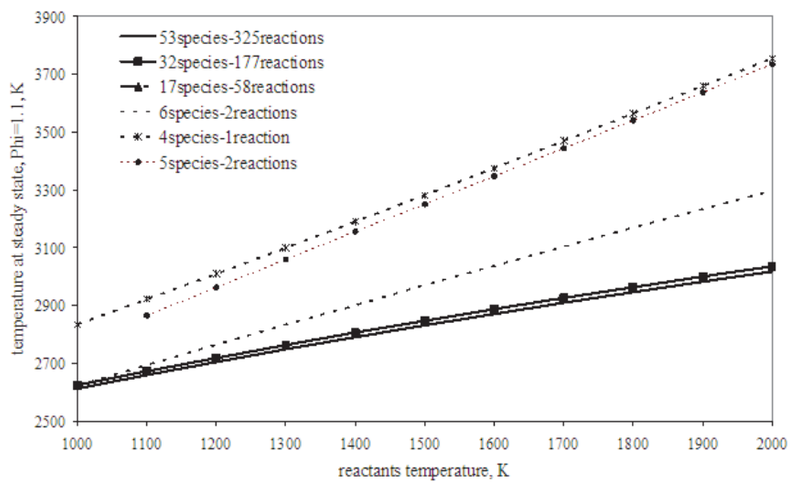


Fig. A6. Φ=1.1, P=3atm, temperature

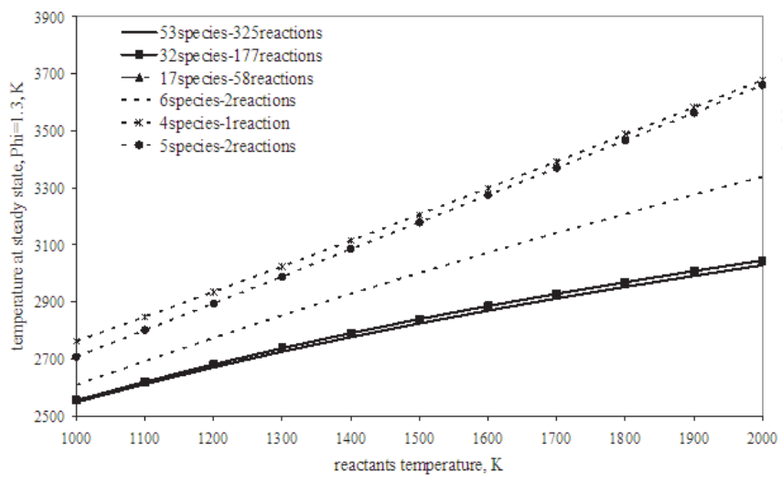


Fig. A7. Φ=1.3, P=3atm, temperature

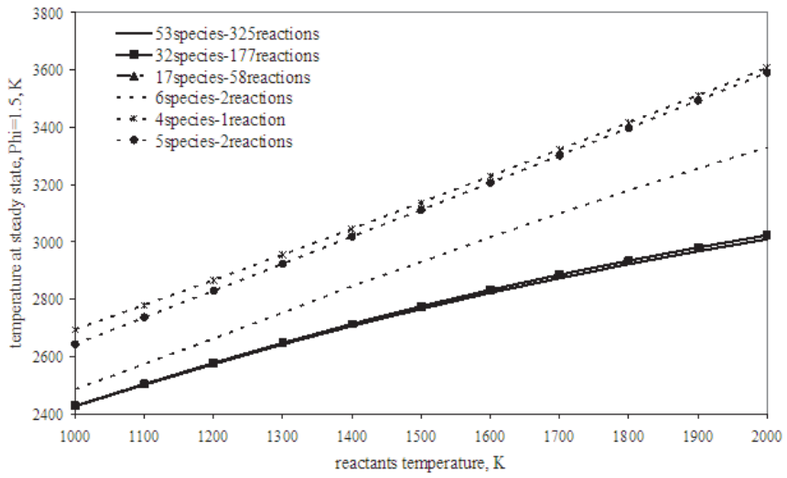


Fig. A8. Φ=1.5, P=3atm, temperature

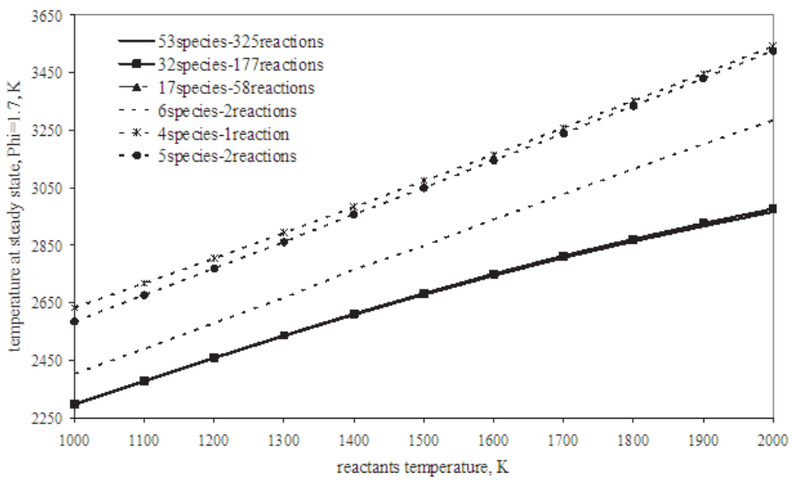


Fig. A9. Φ=1.7, P=3atm, temperature

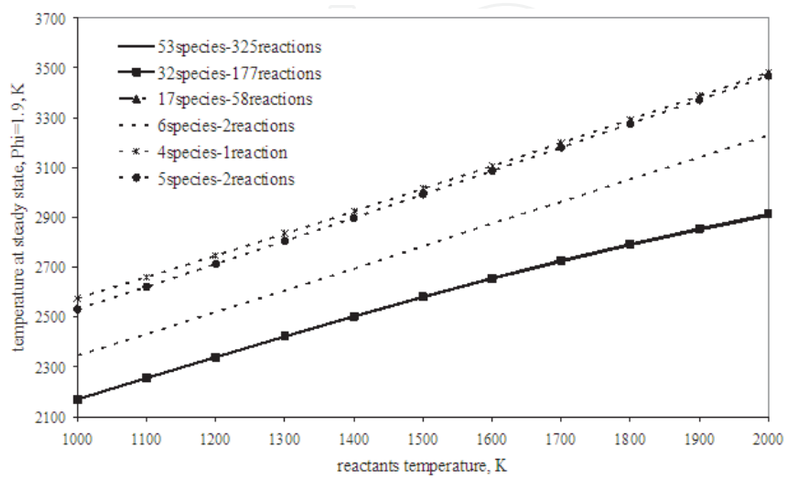


Fig. A10. Φ=1.9, P=3atm, temperature

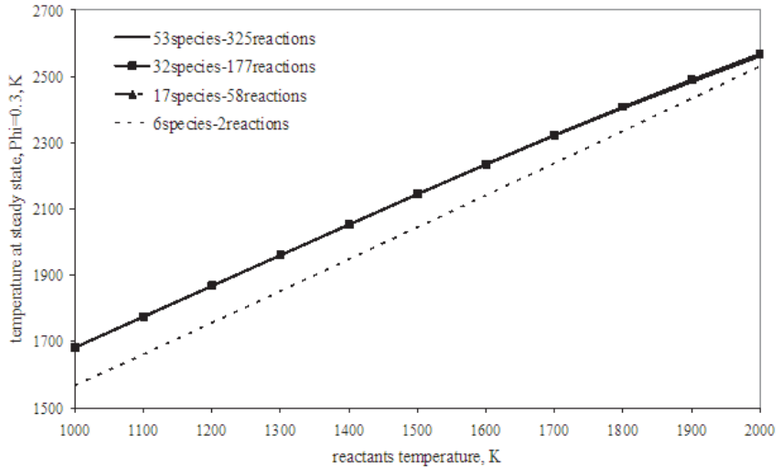


Fig. A11. Φ=0.3, P=5atm, temperature

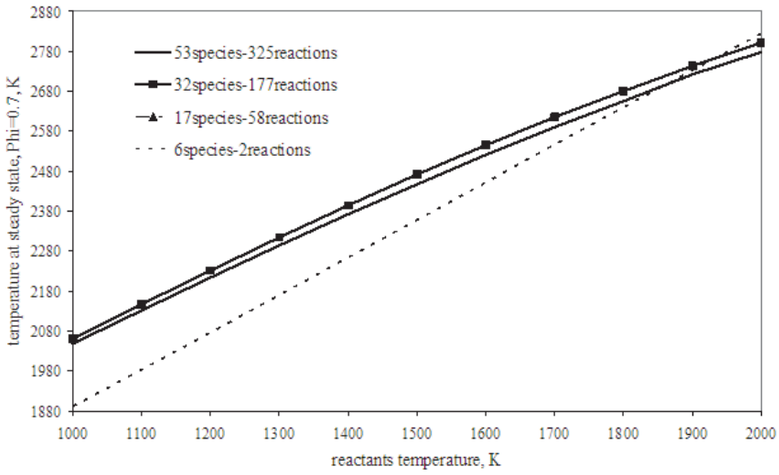


Fig. A12. Φ=0.5, P=5atm, temperature

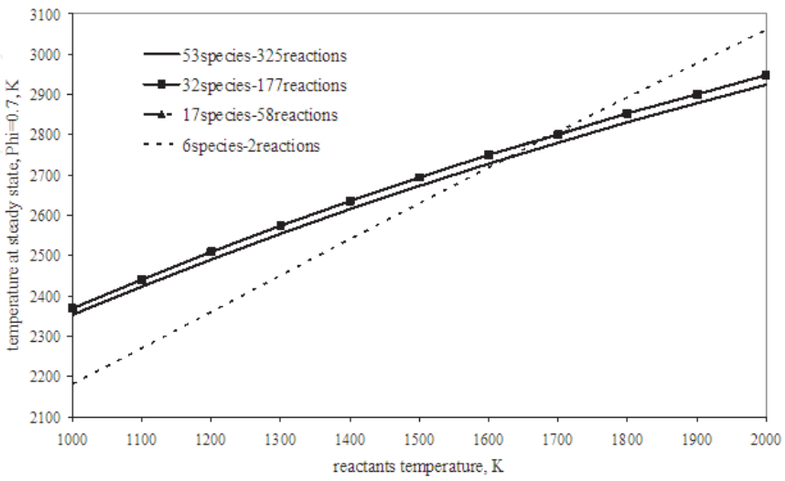


Fig. A13. Φ=0.7, P=5atm, temperature

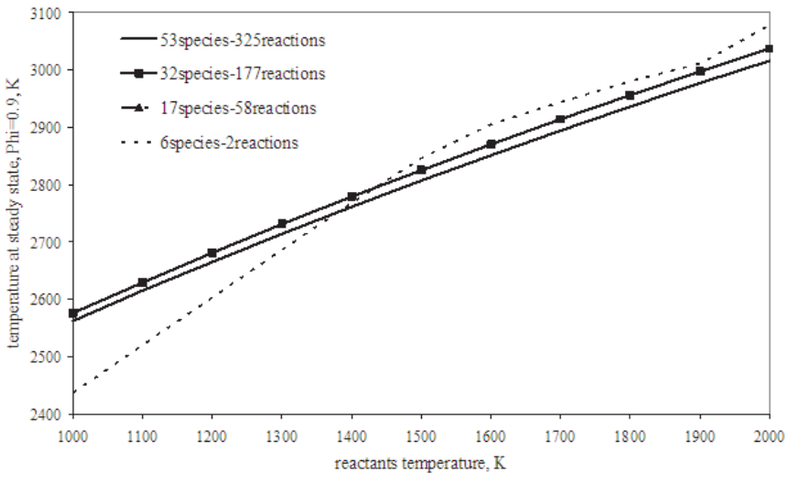


Fig. A14. Φ=0.9, P=5atm, temperature

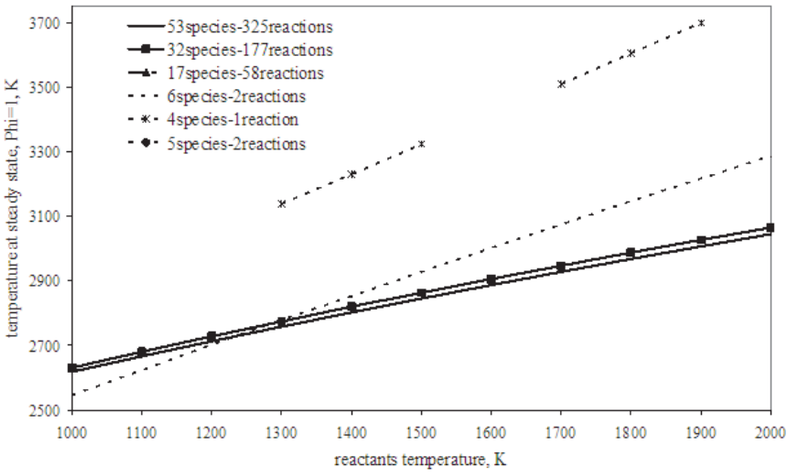


Fig. A15. Φ=1, P=5atm, temperature

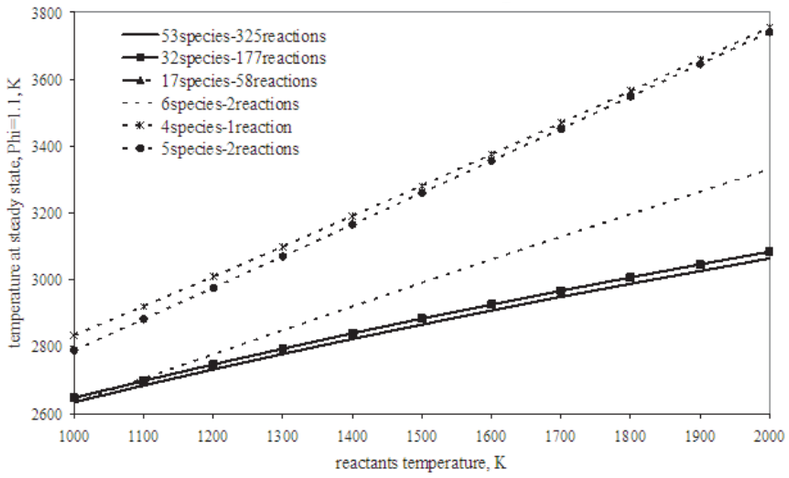


Fig. A16. Φ=1.1, P=5atm, temperature

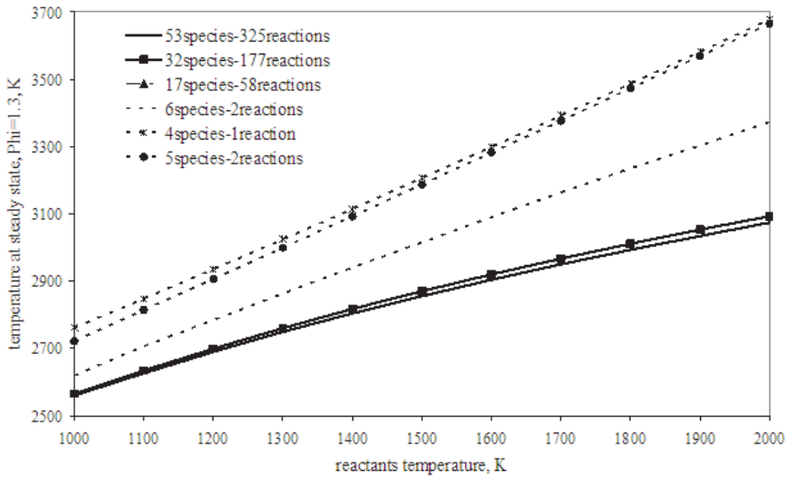


Fig. A17. Φ=1.3, P=5atm, temperature

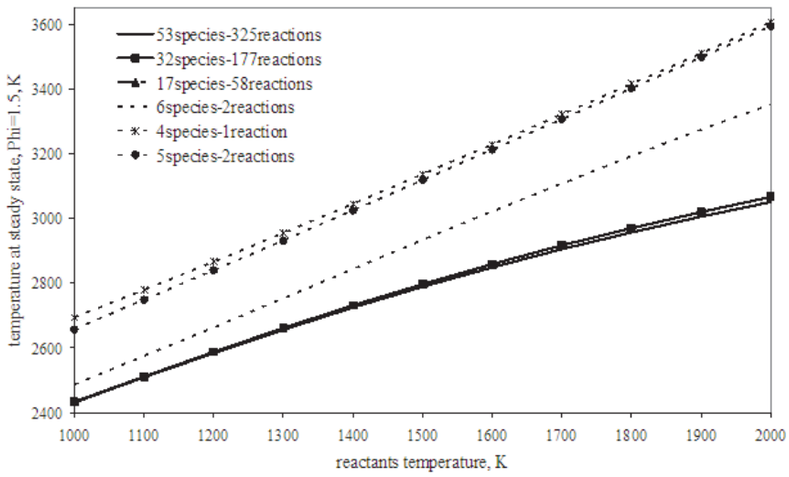


Fig. A18. Φ=1.5, P=5atm, temperature

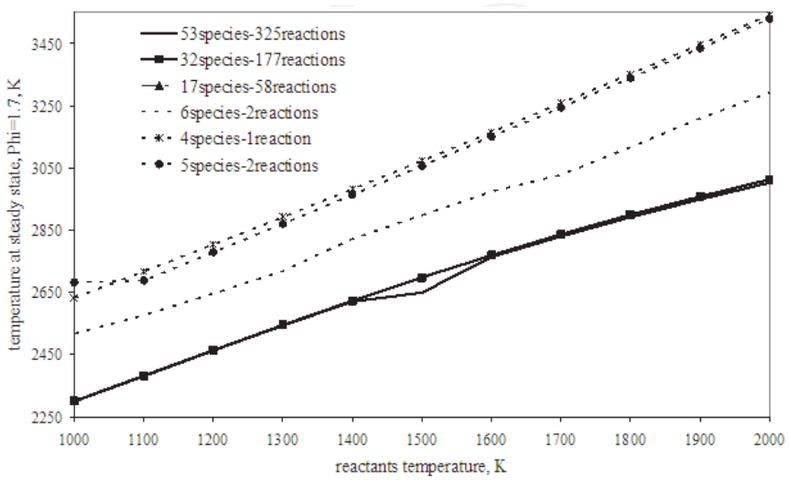


Fig. A19. Φ=1.7, P=5atm, temperature

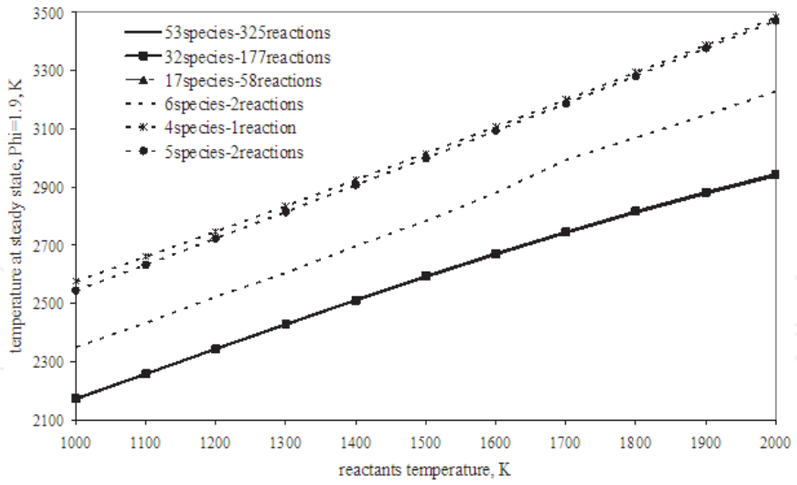


Fig. A20. Φ=1.9, P=5atm, temperature

8. References

Arione, L. (2010) "Development status of the LM10-MIRA engine for the LYRA Launch Vehicle", Proceedings of the "Space 2010" Conference, San Sebastian.

Bowman, C.T. (1986) Chemical Kinetics Models for Complex Reacting Flows, Ber. Bunsenges. Phys. Chem. 90, 934.

Bruno, C. (2001) "Chemical Microthrusters: Effect of Scaling on Combustion", AIAA Paper 2001-3711, AIAA JPC, Salt Lake City.

Bruno, C. (2003) Giacomazzi, E., Ingenito, A. Chemical Microrocket: Scaling and Performance Enhancement, EOARD Contract FA8655-02-M034, SPC 02-4034 Final report, London, UK.

Cozzi, F. (2007) Experimental Analysis of a Swirl Flow in a meso-scale combustor by LDV, XV A.I.VE.LA National Meeting, Milano, Italy.

Cozzi, F., Caratti, L. (2007) Temperature measurements by Spontaneous Raman Scattering in a meso-scale combustor, XV A.I.VE.LA National Meeting, Milano, Italy.

Cozzi, F., Coghe, A., Olivani, A., Rogora, M. (2007): Stability and Combustion Efficiency of a Meso-Scale Combustor Burning Different Hydrocarbon Fuels, 30th Meeting on Combustion, Ischia, Naple, Italy.

Dagaut, P., Boettner, J-C., Cathonnet, M. (1991) Methane Oxidation: Experimental and Kinetic Modeling Study, Combust. Sci. and Tech. 77, pp. 127-148.

DeGroot, W.A., and Oleson, S.R., (1996), "Chemical Microthruster Options", AIAA Paper 96-2863, presented at the AIAA Joint Propulsion Conference, Buena Vista, FL.

Gardiner, W.C. Jr. (1999) Gas-Phase Combustion Chemistry, Springer-Verlag, pp. 31-41.

GRI-Mech Version 1.2 released 11/16/94, http://www.me.berkley.edu/gri_mech/

GRI-Mech Version 3.0 released 07/30/99, http://www.me.berkley.edu/gri_mech/

Hurlbert, E., Angstadt, T., Villemarette, M., Collins, J., Allred, J., Mahoney, J., Peters, T., (2008) 870 lbf Reaction control system test using Lox/Ethanol and LOx/Methane at white sands test facility, AIAA 2008-5247, Hartford.

Heffington, W.M., Parks, G.W., Salzman, K.G.P., Penner, S.S. (1997) Studies of Methane Oxidation Kinetics, 16th Symp. (Int.) Combust. [Proc.], 997.

Hautman, D.J., Dryer, F.L., Shug, K.P., Glassman, I. (1981) A Multiple Step Overall Kinetics Mechanism for the Oxydation of Hydrocarbon, Combust. Sci. Technol. 25, 219.

Kawashima, H., Okita, K., Aoki, K., Azuma, N., Kumawaka, A., Onodera, T., Yoshida, S., Negeshi, H., Manako, H., Koganezawa, T. (2009) "Combustion and regenerative cooling characteristics of LOx/Methane engine", Transactions of the Japan Society for Aeronautical and Space Sciences, Space Technology Japan, Vol. 7, ists 26 (ISTS Special Issue: Selected papers from the 26th International Symposium on Space Technology and Science), pp Ta_7-Ta_11

Kee, R.J., Grcar, J.F., Smooke, M.D., Miller, J.A. (1985) A Fortran Program for Modeling Steady Laminar One-Dimensional Premixed Flames, Report No. SAND85-8240, Sandia National Laboratories.

Janson, S.W., (1994), "Chemical and Electric Micropropulsion Concepts for Nanosatellites", AIAA paper 94-2998, presented at the AIAA Joint Propulsion Conference, Indianapolis.

Minotti, A., Bruno, C., Cozzi, F. (2009) Numerical Simulation of a Micro Combustion Chamber, AIAA Aerospace Science Meeting and Exhibit, Orlando, FL, AIAA-2009-0447.

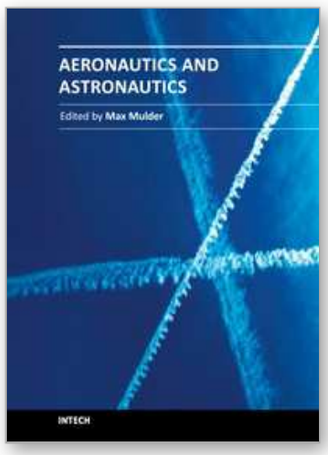
Mueller, J., (1997), "Thruster Options for Microspacecraft: A Review and Evaluation of Existing Hardware and Emerging Technologies", AIAA Paper 97-3058, presented at the AIAA Joint Propulsion Conference, Seattle, July 1997.

Paczko, G., Lefdal, P.M., Peters, N. (1988) Reduced Reaction Schemes for Methane, Methanol and Propane Flames, 21st Symp. (Int.) Combust. [Proc.], 739.

Stone, R., Tiliakos, N., Balepin, V., Tsai, C.-Y., Engers, R. (2008) "Altitude testing of LOx-Methane Rocket engine at ATK-GASL", AIAA 2008-3701, Seattle.

Trevino, C., Mendez, F. (1992) Reduced Kinetic Mechanism for Methane Ignition, 24TH Symp. (Int.) on Combust., The Combust. Inst., pp.121-127

Westbrook, K. C., Dryer, L. F. (1981) Simplified reaction mechanism for the oxidation of hydrocarbon fuels in flames, Combustion Science and Technology 27, pp. 31-43.



Aeronautics and Astronautics

Edited by Prof. Max Mulder

ISBN 978-953-307-473-3
Hard cover, 610 pages
Publisher InTech
Published online 12, September, 2011
Published in print edition September, 2011

In its first centennial, aerospace has matured from a pioneering activity to an indispensable enabler of our daily life activities. In the next twenty to thirty years, aerospace will face a tremendous challenge - the development of flying objects that do not depend on fossil fuels. The twenty-three chapters in this book capture some of the new technologies and methods that are currently being developed to enable sustainable air transport and space flight. It clearly illustrates the multi-disciplinary character of aerospace engineering, and the fact that the challenges of air transportation and space missions continue to call for the most innovative solutions and daring concepts.

InTech Europe
University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China
Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

IntechOpen