VALIDATION OF DETAILED REACTION MECHANISMS FOR SIMULATIONS OF COMBUSTION SYSTEMS WITH GAS INJECTION

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Abstract. This paper concerns the adequacy of existing detailed reaction mechanisms for use in computer simulations of combustion systems with injection of gaseous fuels such as hydrogen, and methane. Shock tube induction time data are compiled from the literature and compared to thermodynamic conditions of gas combustion systems to establish validation limits. Existing detailed reaction mechanisms are then used in constant-volume explosion simulations for validation against the shock tube data. A quantitative measure of mechanism accuracy is obtained from the validation study results, and deficiencies in the experimental data and reaction mechanisms are highlighted.

1. Introduction

Computational simulations are extensively used to study gasdynamics and chemistry of combustion in IC engines. The gasdynamics are given by the Navier-Stokes equations and are coupled to the chemistry through a reation mechanism which specifies how the chemical species evolve. One, two or three step models of the global chemical behavior represent the most simplistic mechanisms. Detailed reaction mechanisms consisting of a comprehensive set of species and reaction rates are the most realistic, attempting to represent all chemical processes within a given system. In between are reduced reaction mechanisms derived systematically from detailed reaction mechanisms.

Simulations of steady one-dimensional flow model with detailed reaction mechanism have been possible for many years. Unsteady, one-dimensional and two-dimensional simulations are beginning to use the smallest detailed reaction mechanism while most unsteady and all multi-dimensional simulations resort to the less complex mechanisms. Given significantly increased computational power over time, these higher fidelity simulations will also incorporate detailed reaction mechanisms. Confidence must be established in the accuracy of all computational simulations through validation with experimental data.

In this paper we consider the adequacy of existing detailed reaction mechanisms for use in combustion systems with gas fuel injection, such as IC engines. Shock tube induction time data are

compiled from the literature and compared to thermodynamic conditions in engines to establish validation limits. Existing detailed reaction mechanisms are then used in constant volume explosion simulations for validation against the shock tube data.

2. Shock tube experiments

Chemical reaction experiments in shock tubes may represent the type of initial and thermodynamic conditions associated with CI gas engines. Data from such experiments often include a measurement of the chemical induction time of the shocked mixture. The induction time is quantitatively defined as the initial thermally neutral period of free radical species concentration growth, beginning with shock heating and compression of the fluid particle and ending with the onset of thermal explosion.

A database of shock tube induction time measurements has been compiled for hydrogen, ethylene, methane, propane, ethane, benzene and toluene oxidation (Teodorczyk, 2001). Data taken from the literature for inclusion in the database met the following criteria: the induction time definition and two thermodynamic state variables corresponding to each induction time data point are provided. The conditions spanned by the experimental data are summarized in Table 1.

2.1. Hydrogen and Methane Shock Tube Data

The hydrogen and methane oxidation shock tube data sets are summarized in Tables 2 and 3. An induction time versus temperature plot for all the data for hydrogen and methane are shown in Figs.1 and 2, respectively. Figures presented in the work of Teodorczyk (2001) contain the induction time data grouped according to data sets in the order given by Tables 2 and 3.

3. Detailed Reaction Mechanisms

The detailed reaction mechanisms considered along with the associated number of species, number of reactions and fuel applicability are summarized in Table 4. Fuel applicability does not necessarily imply that the mechanism was originally intended for use in simulation with a particular fuel but only that the mechanism contains that fuel as a species. The compiled mechanisms and thermodynamic data were summarized in the computer data base which was included in the work of Teodorczyk (2001).

Table 1

Summary of experimental data from shock tubes

Mixture	Data sets	Points	Φ	% of inert	P [MPa]	T [K]
$H_2/O_2/Ar/N_2$	14	940	0,06 – 9,0	0 – 99,9	0,015 - 8,7	775 - 2650

CH₄/O₂/Ar	10	760	0,2 – 3,0	73 – 99	0,02 – 1,6	900 – 2600

Table 2

Induction times for H₂ oxidation in shock tubes

Author	Method	Mixture	Φ	% of inert	P [MPa]	T [K]	End of induction period
Asaba (1965)	Incident	H₂/O₂/Ar	0,085-1,5	96-99	0,02-0,05	1400-2400	OH absorption and luminosity onset
Belles (1965)	Incident	H₂/O₂/N₂	0,125-0,595	63-75	0,02-0,05	1100-1900	OH emission maximum
Bhaskaran (1973)	Reflected	H₂/O₂/N₂	1,0	55,6	0,25	800-1400	Pressure rise and luminosity onset
Cheng (1977)	Incident	H₂/O₂/Ar	0,5-1,0	90	0,1-0,3	1000-1800	Pressure rise onset
Cohen (1967)	Reflected	H₂/O₂/Ar	1,0-2,0	0-94	0,025-0,83	900-1650	UV emission and pressure maximum, UV absorption
Craig (1966)	Reflected	H₂/O₂/N₂	1,0	55,6	0,1-0,2	875-1000	OH emission onset
Fujimoto (1963)	Reflected	H₂/O₂/Ar	1,0	70	0,088-0,27	800-1400	Luminosity and pressure rise onset
Jachimowski (1971)	Incident	H₂/O₂/Ar	0,063-2,0	91-95	0,02-0,075	1200-1800	5% of OH absorption
Just (1968)	Reflected	H₂/O₂/N₂	0,1-1,0	55-76	0,04-0,14	900-1250	Luminosity onset
Petersen (1996)	Reflected	H₂/O₂/Ar	1,0	97-99,9	3,3-8,7	1100-1900	Maximum rate of change of OH absorption
Schott (1958)	Incident and reflected	H₂/O₂/Ar	0,125-9,0	75,3-98,9	0,015-0,95	1050-2650	OH absorption onset
Skinner (1966)	Reflected	H₂/O₂/Ar	2,0	90	0,5	900-1100	OH emission maximum
Snyder (1965)	Reflected	H₂/O₂/N₂	0,5-1,0	55,6-65,3	0,1-0,9	800-1100	Pressure rise and UV emission onset
Steinberg (1955)	Reflected	H₂/O₂	1,0	0	0,45-0,9	700-1000	Luminosity onset

Table 3

Induction times for CH₄ oxidation in shock tubes

Author	Method	Mixture	Φ	% of inert	P [MPa]	T [K]	End of induction period
Burcat (1971)	Reflected	CH₄/O₂/Ar	1	76,9	0,024	1500-1900	Pressure rise and luminosity onset
Cheng (1984)	Reflected	CH₄/O₂/Ar	0,5	90	0,138-0,233	1400-2100	Pressure rise and luminosity onset
Hidaka (1982)	Reflected	CH₄/O₂/Ar	0,1-1	89,5-98,5	0,02-0,038	1700-2300	Pressure rise and luminosity onset
Frank (1987)	Reflected	CH₄/O₂/Ar	0,5-2	95-99	0,2-0,44	1000-2600	Pressure rise and luminosity onset
Jachimowski (1974)	Reflected	CH₄/O₂/Ar	0,8-1,19	91-95	0,116-0,173	1800-2600	Pressure rise and luminosity onset
Lifshitz (1971)	Reflected	CH₄/O₂/Ar	0,5-2	86-97	0,27-1,143	1500-2100	Pressure rise and luminosity onset
Seery (1970)	Reflected	CH₄/O₂/Ar	1	72,7	0,16-0,24	1400-1800	Pressure rise and luminosity onset
Spadaccini (1994)	Reflected	CH₄/O₂/Ar	0,45-1,25	81-90	0,3-0,47	1300-1700	Pressure rise and luminosity onset
Skinner (1987)	Reflected	CH₄/O₂/Ar	0,85-3	90	0,5-1,6	900-1800	Pressure rise and luminosity onset
Tsuboi (1974)	Reflected	CH₄/O₂/Ar	0,2	98	0,34-0,41	1700-2100	Pressure rise and luminosity onset

4. Constant Volume Explosion Simulations

The constant volume explosion model is used to simulate all of the shock tube experimental

conditions with all applicable reaction mechanisms. The numerical and experimental induction times are compared to evaluate reaction mechanism performance. The simulations were carried out with a computer program incorporating the thermodynamic data and detailed reaction mechanisms through the Chemkin II chemical package (Kee, 1989) and the ddebdf integrator (Shampine, 1979) for systems of stiff ordinary differential equations.

Table 4

Detailed mechanisms of chemical reactions

| Author	Species	Reactions	H_2	CH_4	C_2H_2	C_2H_4	C_2H_6	C_3H_8	C_6H_6	C_7H_8
Battin-Leclerc (1997)	63	439	Yes	Yes	Yes	Yes	Yes	Yes	No	No
Baulch (1994)	42	167	Yes	No	No	No	No	No	No	No
Bittker (1987)	39	120	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Bowman (1995) – GRI v.2.11	49	279	Yes	Yes	Yes	Yes	No	No	No	No
Dagaut (1998)	112	688	Yes	Yes	Yes	Yes	Yes	Yes	No	No
Emdee (1992)	33	130	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Frenklach (1994, 1995) – GRI v.1.2	32	177	Yes	Yes	Yes	Yes	No	No	No	No
Glassman (1996)	83	516	Yes	Yes	Yes	Yes	Yes	Yes	No	No
Konnov (1998)	121	1027	Yes	Yes	Yes	Yes	Yes	Yes	No	No
Lutz (1988)	39	154	Yes	Yes	Yes	Yes	No	No	No	No
Maas (1988)	10	37	Yes	No	No	No	No	No	No	No
Miller (1989)	53	235	Yes	Yes	Yes	Yes	No	No	No	No
Philling (1996a)	37	190	Yes	Yes	Yes	Yes	No	No	No	No
Philling (1996b)	10	46	Yes	No	No	No	No	No	No	No
Philling (1998)	56	353	Yes	Yes	Yes	Yes	No	No	No	No
Tan (1994)	82	508	Yes	Yes	Yes	Yes	Yes	Yes	No	No
Wang (1997) – GRI v.2.11mod	34	192	Yes	Yes	Yes	Yes	No	No	No	No
Wang (1999)	385	1896	Yes	Yes	Yes	Yes	Yes	Yes	No	No
Warnatz (1997)	34	164	Yes	Yes	Yes	Yes	No	No	No	No
Westbrook (1982)	29	93	Yes	Yes	Yes	Yes	Yes	Yes	No	No
Westbrook (1984)	36	168	Yes	Yes	Yes	Yes	Yes	Yes	No	No
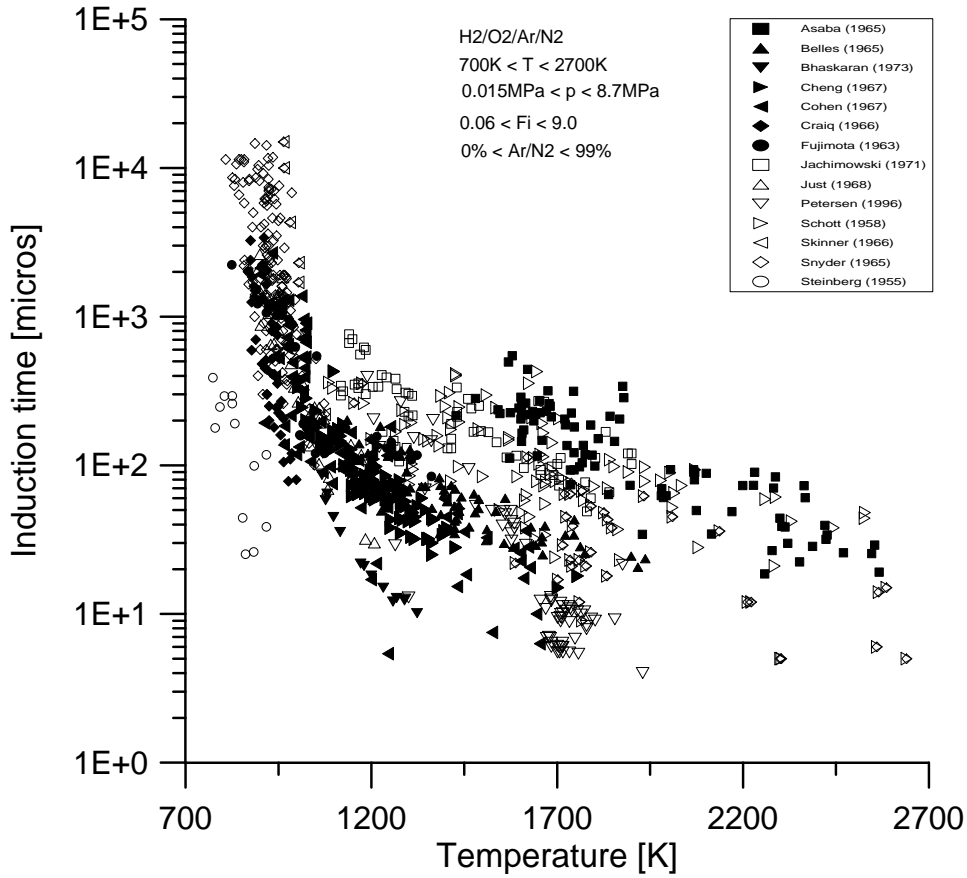
Fig.1. *Induction times for hydrogen oxidation versus temperature. Experimental data from shock tubes*

The program evolves the energy and species equations through time for an adiabatic, fixed-volume fluid particle:

$$\frac{de}{dt} = 0$$

$$\frac{dy_i}{dt} = \Omega_i$$

The initial energy for an ideal gas is related to the temperature and species through a caloric equation of state:

$$e = e(T, \widehat{y}) = \sum_{i=1}^{K} y_i e_i(T)$$

The internal energy of each species as a function of temperature is calculated with NASA polynomial functions from the thermodynamic database supplied with Chemkin. Taking the differential of this expression gives:

$$de = \sum_{i=1}^{K} dy_i e_i + dT \sum_{i=1}^{K} y_i \frac{de_i}{dT} = \sum_{i=1}^{K} dy_i e_i + dT \sum_{i=1}^{K} y_i c_{v,i} = \sum_{i=1}^{K} dy_i e_i + c_v dT$$

where c_v is the average constant volume heat capacity for the mixture. Substituting into the

original energy equation for the internal energy differential, the energy equation is re-formulated in terms of temperature:

$$c_v \frac{dT}{dt} = -\sum_{i=1}^{K} \frac{dy_i}{dt} e_i = -\sum_{i=1}^{K} \Omega_i e_i$$

The species mass fractionproduction rate is calculated through Chemkin subroutines with the reaction mechanism providing the reaction rate constants in the standard form of:

$$k_i = A_i T^{n_i} \exp\left(-\frac{E_i}{RT} \right)$$

Detailed discussion on the various forms of reaction rate expressions is provided by Kee (1989). The initial conditions for each simulation consisted of the gas mixture composition, post-shock pressure, and post-shock temperature.

The evolution of temperature, power, and some species for a representative constant-volume explosion simulation are presented in Figs.4 and 5. Hydrogen and oxygen are consumed through the reaction zone while hydroxyl is the intermediate radical species and formation of the water product is the primary exothermic reaction.

The induction times computed from constant-volume explosion simulations were compared to the experimental shock tube data. The computational results for hydrogen oxidation with the use of several kinetic mechanisms are shown in Fig.5. Figure 6 presents comparison of computed ignition delay times using Lutz (1988) mechanism with the experimental data of Belles (1965). Figure 7 shows computed results for methane oxidation with th euse of four kinetic mechanisms.

Simulations with all mechanisms clearly indicate a general tendency for the simulations to overpredict the experimental induction times. High temperatures also correspond to the regime of short induction times, less experimental uncertainty, improved applicability of the constant volume explosion model.
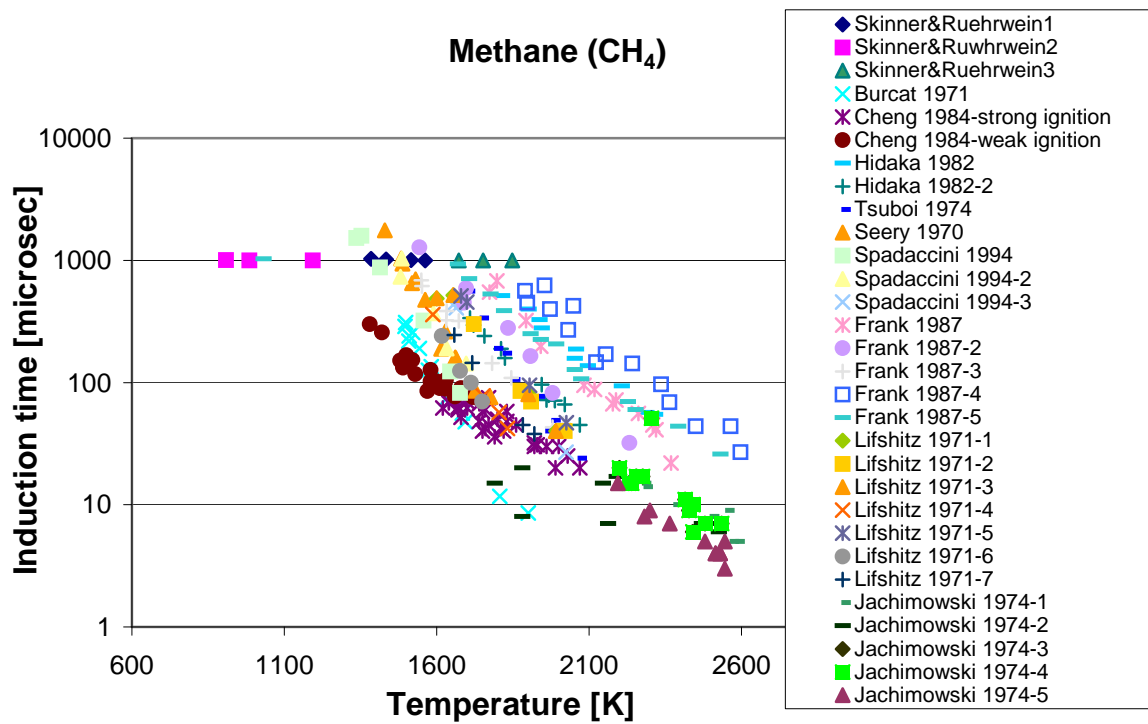
Methane (CH₄)

Fig. 2. *Induction time for methane oxidation as a function of temperature. Experimental data from shock tubes*
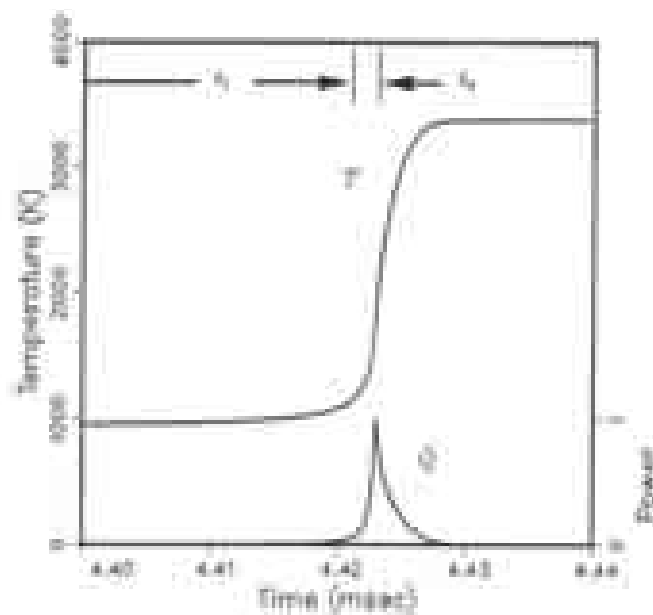

Fig. 3. *Temperature and nondimensional chemical power for stoichiometric hydrogen-oxygen mixture during autoignition at constant volume. Initial conditions: 950 K and 1 atm. Induction time t_i = 4,421 ms; excitation time t_e = 2,0 μs. Power is normalized to maximum value: $3 \cdot 10^9$ wg*
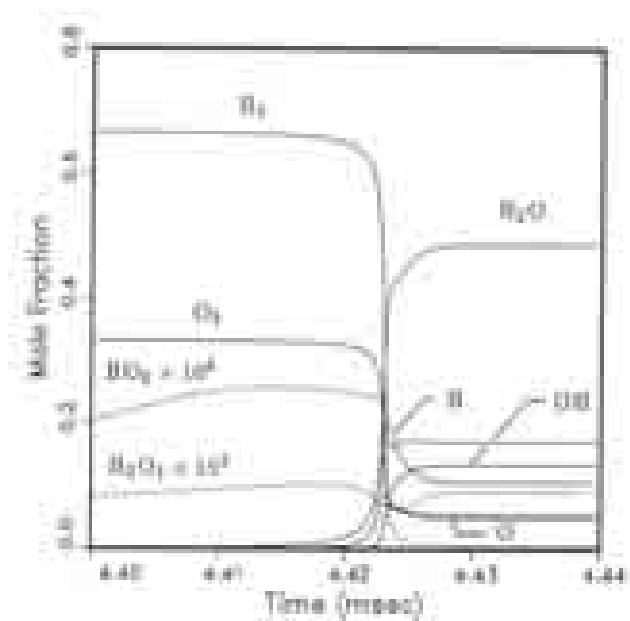
Fig. 4. *Composition of hydrogen-oxygen mixture during autoignition shown in Fig 1. Dotted line shows components the molar fractions of which were increased to show in this scale*
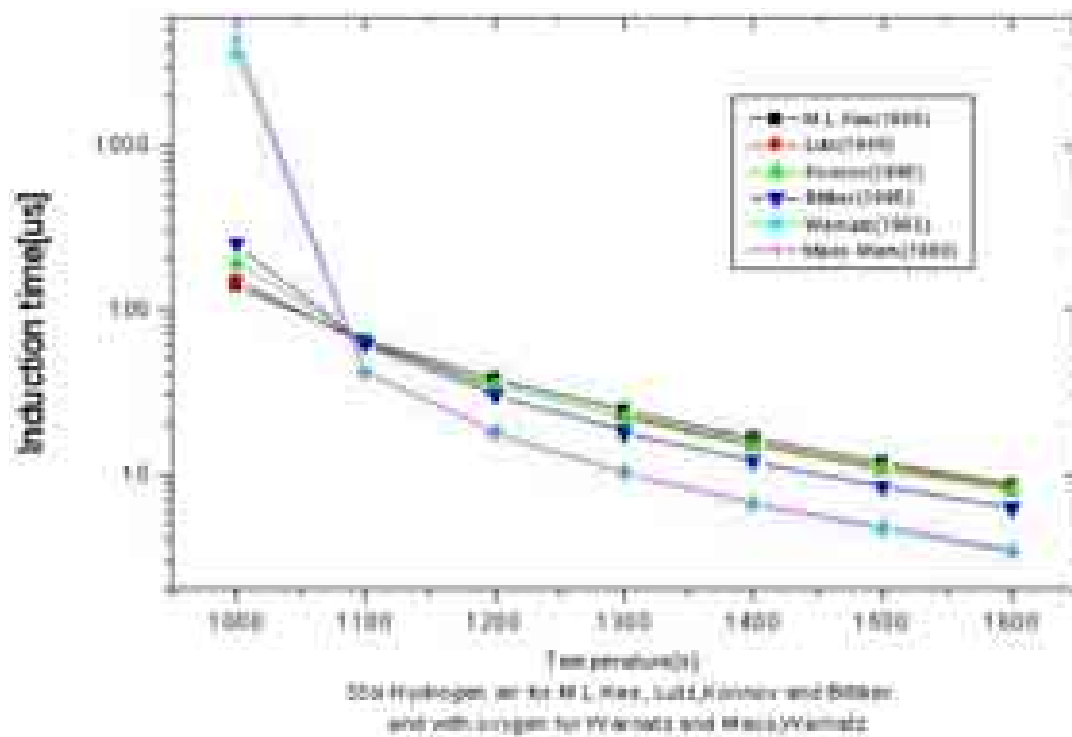

Fig. 5. *Calculated induction time vs temperature for hydrogen oxidation*
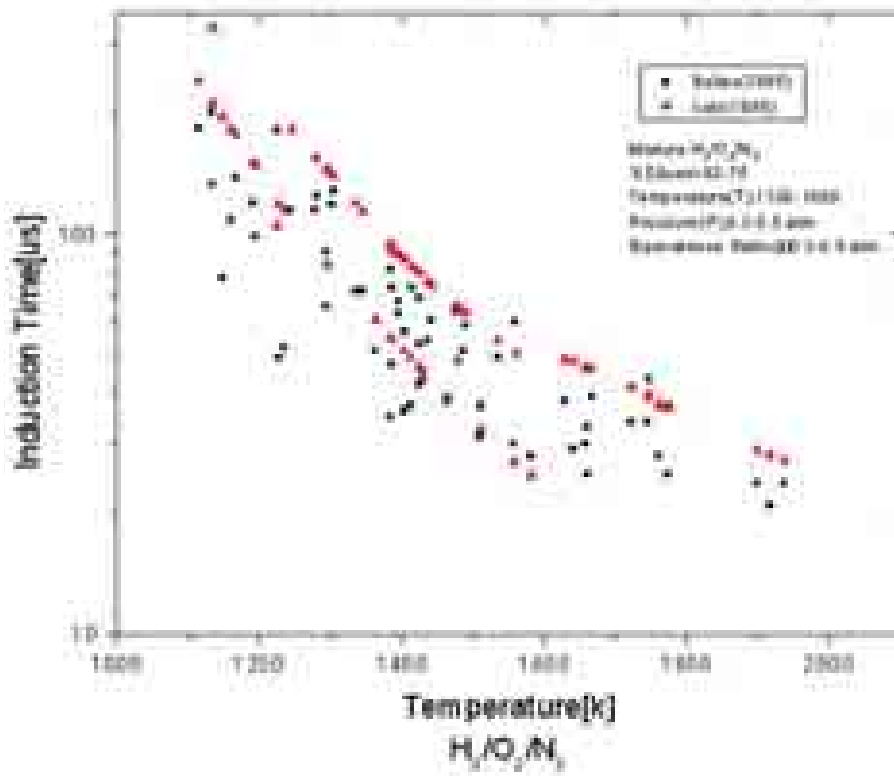
Fig. 6. *Comparison of calculated (Lutz mechanism) and experimental values (Belles) of induction time vs temperature for hydrogen oxidation*
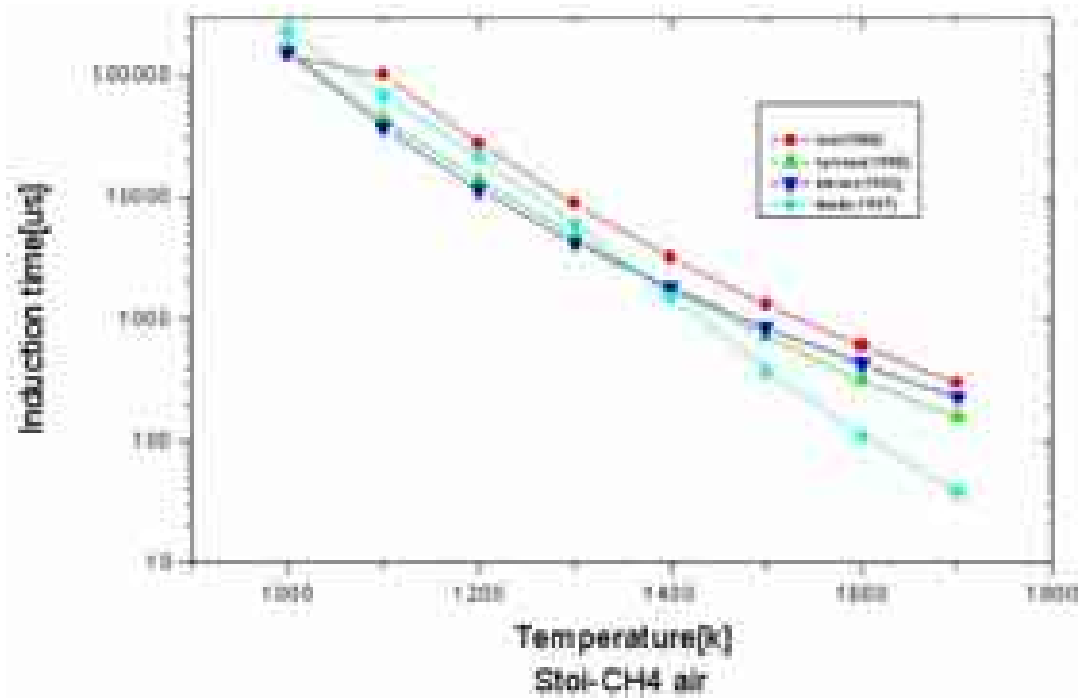

Fig. 7. *Calculated induction time vs temperature for methane oxidation*

Conclusions

Shock tube induction time data for hydrogen and methane oxidation were compiled from literature. Existing detailed reaction mechanisms were then used in constant-volume explosion simulation for validation against the shock tube data. A quantitative measure of mechanisms accuracy was obtained from the validation study results.

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