Updated (high H_2/CO contents) Kinetic Mechanisms

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Abstract

The report proposes to deliver the output of the present milestone M.1.3. The report includes a review of the recent models for high H2/CO contents kinetic mechanisms with the analysis of the deficiencies that remain. The updated mechanism is presented with a discussion on the choice of the rate constants. Validation of the mechanism is done using experimental data on flame speeds and ignition delays available in literature and most relevant to gas turbine conditions.

The updated H2/CO combustion mechanisms are presented with their evaluation of predictive capability for flame speed. The contemporary choice of the reaction rate constants is presented with the emphasis on their uncertainties and the predictions of ignition, oxidation, flame burning velocities and flame structure of H2/CO - oxygen - inert mixtures are shown. Particular attention was paid to pressure dependence of reaction between CO and OH.

Modeling range covers ignition experiments from 950 to 2700 K from subatmospheric pressures up to 87 atm for hydrogen combustion; hydrogen oxidation in a flow reactor at temperatures around 900 K from 0.3 up to 15.7 atm; flame burning velocities in hydrogen - oxygen - inert mixtures from 0.35 up to 4 atm; hydrogen flame structure at 1 and 10 atm. Range for hydrogen/carbon monoxide combustion varies from atmospheric to 20 atm and equivalence ratio from 0.3 to 1. Comparison of the modeling and experiments is discussed in terms of the range of applicability of the present detailed mechanism. A necessity of the analysis of the mechanism having exhaustive list of reactions was emphasized.

Introduction

One of the most recent and advanced technology for high-efficiency gasification of fossil fuels or biomass is the Integrated Gasification Combined Cycle (IGCC) power generation systems. The process includes conversion of coal into a synthesis gas(syngas) in a gasifier. The gas is composed of primarily Hydrogen and carbon monoxide and smaller amount of carbon dioxide and steam. This technology includes the capturing of CO_2 by pre-combustion methods (Carbon capture and storage, CCS) combined with low emissions of other gases like NO_x, and SO_x. Since reactivity of hydrogen is much higher than natural gas, it is complicated to apply premix burners and hence diffusion burners are used. Syngas is diluted with N_2 or water to have lower adiabatic flame temperatures.

A kinetic mechanism has an important role in the development of this kind of advanced combustion technologies that aims to the production of hydrogen rich syngas fuel. Simulation of the reacting flows is the basis for designing the combustors. The kinetic mechanism is one of the key tools in predicting entities like flame speed and ignition delay for implementation in commercial CFD codes. Hence, it is of utmost importance to analyze the kinetics of each reaction, their behavior at different conditions of pressure, temperature and fuel/oxidizer composition and implication on the production of other species. The present work gives an updated list of rate constants for the reactions relevant for H_2/CO reacting systems at conditions that are relevant to gas turbine combustion.

Several studies have been made with respect to counter-flow and spherically expanding flames of H_2/CO mixtures for stoichiometric and rich conditions. The above mentioned gas turbine technology requires lean combustion. Also, high pressure and low flame temperature are employed to increase efficiencies and reduce NO_x emissions respectively. Even the most recent kinetic models have great difficulty in predicting flame speeds at high pressure and low flame temperature conditions. These conditions are most relevant for syngas combustion in gas turbines. There is a region where flame properties are strongly sensitive to a number of reactions that have large uncertainties in their temperature and pressure dependence. Among the most recent work Burke et al. [1] measured burning rates for H_2/CO/O_2/diluents flames, analyzed their key reactions and kinetic pathways with the same intention of providing data for modeling reaction mechanism for syngas combsution. Natarajan et al. [2] measured flame speed with a conical flame stabilized on a contoured nozzle for 50:50 H_2/CO till 15 atm with O_2:He (1:7 and 1:9 by volume) mixture as oxidizer and equivalence ratio from 0.6 to 1.2.Ignition delay is another parameter often used for validating reaction mechanism. Coupling of a reliable kinetic mechanism with a numerical flow solver accurately models reacting flow problems. Considerable amount of work has been done in analyzing differences in experimental data and predictions using kinetic models. Experimental data are drawn from shock tube, flow reactor and rapid compression experiments. These and many such studies have revealed disagreement between experimental data and model predictions. These experimentations have implied that there exists a lot of scope in improvement of rate constants when compared to flame speed and ignition delay data obtained.

The objective of the present work is to review the most recent high H_2/CO contents kinetic mechanisms, make choices of reaction rate constants to construct an updated mechanism that can take care of the high pressure, low flame temperature and lean conditions of syngas combustion.

Review of the recent models for the high H2/CO contents kinetic mechanisms

It is a well known fact that "dry" CO - O_2 mixture that is mixture without hydrogen-containing additives reacts very slowly since oxidation includes only two steps
$CO+O_2 = CO_2 +O$
$CO+O+M = CO_2 +M$
But in the presence of traces of hydrogen, water or hydrocarbons chain process develops fast with participation of H, OH, and HO_2 radicals; CO oxidation proceeds mainly through reactions
$CO+OH = CO_2 +H$
$CO+HO_2 = CO_2 +OH$
Comprehensive kinetic schemes of carbon monoxide oxidation in presence of hydrogen-containing additives allow to model ignition limits observed [3], as well as flame propagation speed [4]. Oxidation of $CO/H_2O/O_2$ and H_2/O_2 mixtures in flow reactor was investigated by Yetter et al. [5] at temperature range 852 - 1138 K and mechanism consisted of 28 reactions was suggested [6] for a wide range of experimental conditions (823 - 2870 K, φ = 0.0005 - 6.0, C/H = 0.005 - 128, H = 0.3 - 2.2 atm). It was pointed out that different mechanisms suggested in literature can adequately describe experimental macro-parameters such as ignition delays, rates of fuel consumption and product formation. Yet simplified mechanisms in general cannot be used for calculation of radical concentrations and are restricted to the limits of their direct examination. The reaction composition of submechanism for carbon monoxide oxidation usually depends upon the range of model validity [6,7].

Renewed interest in the combustion characteristics of CO/H_2 mixtures is motivated by the foreseeable increasing application of syngas in energy production [8] and even propulsion [9]. Substantial progress made in accurate determination of the elementary reaction rates and thermodynamic properties as well as in measurement of the integral combustion characteristics such as burning velocities and ignition delays stimulated development of several detailed kinetic mechanisms for the combustion of hydrogen and carbon monoxide mixtures [10-13]. Davis et al. [10] used the H_2/CO sub-mechanism of the GRI-mech. version 3.0 [14] as a starting point and demonstrated that optimization of this model can bring very good agreement with the experiments chosen as targets. Zsely et al. [11] revised H_2/CO reaction set of the Leeds methane oxidation mechanism [15] using the latest CEC evaluations [16]. Particular attention in this work [15] has been paid to the uncertainties of the modeling caused by the uncertainties in the rate constants. Updates of the H_2/CO sub-mechanism have been made by Saxena and Williams [12] and good agreement of the modeling with laminar burning velocities and ignition delay of hydrogen + carbon monoxide mixtures at atmospheric pressures was demonstrated. The mechanism of Davis et al. [10] was further refined by Sivaramakrishnan et al. [9] to improve its agreement with oxidation experiments at intermediate temperatures and very high pressures. Li et al. [13] presented detailed kinetic mechanism for CO, CH_2O, and CH_3OH combustion which included their H2/O2 sub-mechanism [17]. They recommended two new rate constants for H_2/CO submechanism. Sun et al. [18] submitted an updated kinetic mechanism meant to predict flame speeds at higher pressure with the modification in one of the reaction rate constants.

Saxena and Williams [12] restricted the range of applicability of their model to temperatures above 1000 K. The range of experimental conditions covered by the mechanism of Li et al. [13] was stated as from 298 to 3000 K. This does not mean, however, that this model is applicable at low temperatures encountered in atmospheric chemistry of H_2/CO system. For example, effect of pressure on the key reaction between CO and OH well established at low temperatures was not present in the combustion mechanisms cited above. Sivaramakrishnan et al. [9] argued that the addition of a high pressure channel forming HOCO adduct followed by its subsequent decomposition to CO_2 + H cannot improve agreement of their modeling with experiments performed in the range from 1000 to 1500 K. On the other hand Fulle et al. [19] demonstrated that at 819 K pressure dependence of the reaction between CO and OH becomes notable at about 10 atm and higher. The lowest temperature accessible in experiments on syngas ignition was about 600 K [20]. Correct modeling of these experiments therefore requires incorporation of the pressure-dependent rate constant forming HOCO adduct. Moreover, the chemistry of H_2/CO oxidation is a core of any detailed reaction mechanism for combustion modeling including those developed for self-ignition and oxidation of hydrocarbons at intermediate (~600 K and higher) temperatures. This means that proper extension of the hydrogen + carbon monoxide oxidation mechanism down to these temperatures requires bridging a gap between combustion and atmospheric chemistry.

The most recent experimental data from literature suggests that the recent kinetic mechanisms for H_2/CO combustion requires modification. Natarajan et al. [2] performed a study that included measurement of laminar flame speeds of H_2/CO mixtures at elevated pressures, preheat temperatures and lean conditions that are relevant to gas turbine combustors. Over prediction of the temperature dependence of the flame speed for medium and high H_2 content syngas was reported for mechanisms by Davis et al. [10] and Li et al. [13] at very lean conditions. This effect is seen higher at atmospheric pressure than at high pressures. They cited that errors maybe due to the 'low temperature' reactions that become important when temperatures of unburnt gases are increased. Also, Burke et al. [1] performed various experiments on H_2/CO/O_2/diluents fuels for wide range of equivalence ratio, flame temperatures and pressure in a dual-chambered constant volume cylindrical bomb. Disagreement with model predictions of Davis et al [10] and Li et al.[13] at higher pressures for all CO fuel fractions was reported. A modification to several rate constants of reactions in hydrogen submechanism has been suggested.

It is also notable that even the list of reactions of the H_2/CO combustion mechanisms is not always complete. For example, Davis et al. [10] did not include self-reactions between HCO radicals which act as chain-termination

$HCO + HCO = CH_2O + CO$ (35)

$HCO + HCO = CO + CO + H_2$ (36)

Reaction numbering corresponds to the list in Table 3. If these missing reactions have sensitivities comparable with reactions which are present in the model of Davis et al. [10] then the rate constants derived during optimization of the incomplete reaction set could be misleading.

Among the recent work in analyzing ignition delay times predicted using kinetic models is from Mittal et al. [21] where experimental data from rapid compression machine for higher pressures (up to 50bar) and temperature range of 950 to 1100K was used in evaluating mechanism by Davis et al. [10]. They reported discrepancy in the predictions and recommended revision of the rate constant of $CO+HO_2$ reaction. With a modification in the rate constant of the same reaction Walton et al. [8] compared experimental data to the modified version of the mechanism by Davis et al.[10] and reported good agreement but emphasizes that it over predicts the activation energy. The difference was attributed to the large uncertainty involved in the above reaction. Sivaramakrishnan et al [9] performed experiments on shock tube for pressure 21-500 bars and temperature range of 1000-1500K for stoichiometric and lean H_2/CO mixtures. Peterson et al. [20] and Reehal et al. [22] have analyzed that ignition delay data at lower temperatures do not match experiments to a large extent and reported that the differences remain more at lower temperatures than at higher pressures. However, work of Chaos [23] argues that at ignition delay data at the condition of interest do not represent chemical kinetic observation and vary for different facilities of same nature. In order to properly interpret shock tube ignition data pressure/temperature histories must also be provided.

The goal of the present work was therefore to analyze the performance of the H_2/CO mechanism using updated kinetic and thermodynamic data and exhaustive list of reactions for higher pressure and temperature as existing mechanisms still require better rate constants. In the following, the contemporary choice of the reaction rate constants is presented with the emphasis on their uncertainties.

In the present work the mechanism of Konnov [24] was updated taking into account recent evaluated kinetic data for combustion modeling and for atmospheric chemistry. Then the predictions of ignition, oxidation, flame burning velocities and flame structure of hydrogen-carbon monoxide-air mixtures are presented. Comparison of the modeling and experiments is discussed in terms of the range of applicability of the present mechanism.

Table 1: Latest kinetic mechanisms for H_2/CO mixtures

Mechanisms	Year	No. Of Reactions
Sun et al. [18]	2007	33
Li et al. [13]	2006	33
Saxena et al. [12]	2006	30
Davis et al. [10]	2005	30

Analysis of the remaining deficiencies

Over-prediction of flame speeds at higher preheat temperatures : It has been reported from a number of sources from literature that as the preheat temperature of the fuel/oxidizer mixture increases even the most recent models for H_2/CO combustion over predict the flame speed to as much as 35% at very lean conditions for T=700K. The gap between the predicted and measured values widen as the temperature is elevated beyond 500K. Natarajan et al. [2] have reported experiments for a range of lean H_2:CO mixtures (from 20% to 80% H2) for higher pressures and have concluded mechanism by Li et al.[13] is in good agreement. However, the same mechanism showed over prediction for higher pressure and higher preheat temperature at lean condition for a range of H_2:CO compositions. Also, enhanced temperature dependence is less pronounced at high pressure compared to atmospheric pressure. A sensitivity and heat release rate analysis inferred possible errors in three reactions in the H_2 submechanism. Suggestions are made to look into HO_2 radical formation and destruction reaction that has largest contribution to the uncertainty in the predicted flame speed.

Over-prediction of ignition delay times : At temperatures near 700-800K, the measured ignition delay times are as much as two to three orders of magnitude lower than what is predicted by current kinetic models. Calculation by Peterson et al. [20] indicate that uncertainties in the rates of elementary reactions commonly found to be important between and above the second and third explosion limits of H_2/CO oxidation does not entirely explain the discrepancy. Mittal et al. [21] attributes this discrepancy largely to reaction (27).

$$CO + HO_2 = CO_2 + OH \qquad (27)$$

Studies by Sivaramakrishnan et al. [9] revealed strong and peculiar temperature dependence of reaction (17)

$$HO_2+OH=H_2O+O_2 \qquad (17)$$

suggested a sum of modified Arrhenius expressions and reported it would be better if this rate is parameterized by a non Arrhenius expression. Present study utilizes a sum of two expressions. Chaos et al.[23] have reported that kinetic model predictions use homogenous, zero-dimensional, isochoric modeling assumptions typically used for mechanism validation. A constant internal energy and constant volume assumption in the modeling fails to estimate ignition delay at lower temperatures and hence mechanism should not be questioned. For this very reason, CHEMKIN-II [25] is reported to be capable of handling this situation. It is also proposed to use measured pressure histories in modeling approaches rather than using averaged or effective values. Present work therefore focuses more on predicting flame speeds than ignition delay.

Discussion of the choice of the rate constants

The rate constants of the reactions pertinent to hydrogen combustion sub-mechanism have been reviewed by Konnov [24]. At the present stage all these rates have been adopted as is without modifications. Although Burke et al. [1] demonstrated that the mechanism of Konnov [24] disagrees with the most recent measurements in hydrogen flames diluted by helium and argon at pressures above 10 atm further modification in the hydrogen sub-mechanism will require complete re-evaluation run of the modeling. This is our objective for 2010. In the following only reactions pertinent to carbon monoxide chemistry are discussed.

The peculiarities of the rate constant of reaction

$CO + O (+M) = CO_2 (+M)$ (23)

were analyzed by Troe [26], Gardiner and Troe [27], Warnatz [28], and Westmoreland et al. [66]. Allen et al. [29] proposed to combine the low-pressure rate constant expression from Westmoreland et al. (1971) fit to modified Arrhenius form and Troe's [26] high-pressure rate constant using a Lindemann fit [27]. Warnatz et al. [30] modified recommended low-pressure rate constant of Warnatz [28] within 1000 – 3000 K multiplying by a factor of 1.34. Davis et al. [10] evaluated uncertainty factor of this rate as 2, and in the optimization procedure proposed to multiply the rate constant of Allen et al. [29] by a factor of 0.76. In the present work the expression of Allen et al. [29] was adopted with the uncertainty factor of 2.

Temperature and pressure dependence of the rate constant of reaction

$CO+OH = CO_2 +H$ (24)

was a subject of many experimental and theoretical studies. Experimental studies and reviews prior to 2004 were summarized by Baulch et al. [16]. Rate constants derived by Troe (1998) were largely based on the experiments of Fulle et al. [19]. They have been accepted as recommendations by Baulch et al. [16]. The involvement of formation of the intermediate species HOCO and hence pressure and temperature dependence is argued by Troe [31]. Li et al. [13] also acknowledges this fact and determined a rate constant by fitting experimentally measured rate constants available in literature by the method of least squares. Regrettably most of the recent studies are theory. Expression of Li et al. [13] has been adopted.

The rate constant of reaction(25) has been derived based on Troe [26].

$CO + OH (+M) = HOCO (+M)$ (25)

The following reaction is also a source of consumption of CO. The rate constant suggested by Warnatz [28] have been used for the present study.

$CO + O_2 = CO_2 + O$ (26)

The following reaction is influential for CO concentration.

$CO + HO_2 = CO_2 + OH$ (27)

Kim et al. [32] and Tsang and Hampson [33] suggested rate constants that were reported by Sivaramakrishnan et al. [9] to be having uncertainty much higher. This reaction becomes important during the chemical induction period as they have significant heat release at that stage. Through experimental studies Mittal et al. [21] suggested usage of a revised lower value than Baulch et al. [16] especially for temperatures around 1000K. Sun et al. [18] performed calculations based on *ab initio* theory and canonical transition state theory to determine the reaction rate constant which has been used in the present study.

The following decomposition of formyl radical is the main pathway to generation of CO during high temperature combustion.

$HCO + M = H + CO + M$ (28)

Timonen et al. [34] studied the reaction of HCO with four molecules as a function of temperature in a tubular reactor and determined their rate constants. Studies by Li et al. [13] inferred that the rate is two times lower than that of Timonen et al. [34]. Zhao et al. [35] showed that the reaction is most sensitive to certain temperature range. Li et al. recommended a weighted least square fitting to all experimental data available in the literature and yielded a new correlation. Baulch et al. [36] reviewed the rate constants prior to 1992 and recommended a value which is being used in the present study.

The rate constants suggested Tsang and Hampson[33] for the following reactions were comfortably accepted by Baulch et al.[16] and Li et al. [13]. The present work considers the value by Baulch et al. [16] for a wider temperature range.

$HCO + O = CO + OH$ (30)

$HCO + O = CO_2 + H$ (31)

The following equations have rate constants on the reviews and evaluations of Baulch et al. [16].

$HCO + H = CO + H_2$ (29)

$HCO + OH = CO + H_2O$ (32)

$HCO + O_2 = CO + HO_2$ (33)

Two reactions between hydroperoxy radical and formyl radical

$HCO + HO_2 = CO_2 + OH + H$ (34)
$HCO + HO_2 = CO + H_2O_2$ (35)
have not been studied experimentally. Tsang and Hampson [33] estimated total rate constant with high uncertainty of a factor of 5. In the present study this rate was attributed to reaction (34). Second channel was assumed minor with rate 10 times smaller.

Self-reaction between HCO radicals includes two channels
$HCO + HCO = CH_2O + CO$ (36)
$HCO + HCO = CO + CO + H_2$ (37)
In the majority of kinetic studies reviewed by Baulch et al. [16] these channels were indistinguishable and an overall rate constant within 230-1000 K was given with the uncertainty factor of 1.6 at 300 K rising to 2 at 1000 K. For instance, Quee and Thynne [37] assumed 2 CO and H_2 major products and derived from fitting to a complex mechanism a rate constant of 2.19e+13 cm**3/(mol * s). Friedrichs et al. [38] assumed reaction (36) a major channel and demonstrated that at temperatures below 820 K concentration time profiles of HCO are affected by this reaction, therefore it should be considered in kinetic models developed for these intermediate temperatures. In the present study the temperature-independent rate constant of Friedrichs et al. [38] was attributed to reaction (36). Following recommendation of et al. [13] reaction (37) is assumed 10 times slower temperature-independent with somewhat higher uncertainty. This gives total rate constant proposed by Baulch et al.[16].

Reaction (38) derives its rate constant from [69]
$HOCO (+M) = H + CO_2 (+M)$ (38)
This reaction proceeds as an intermediate to the reaction (25). The reaction is temperature dependent over a narrow range of 200-360K..

The rate constant of reaction
$HOCO+OH=H_2O+CO_2$ (39)
has never been measured. Yu et al. [39] performed ab initio dynamic calculations of the thermal rate constant from 250 to 800 K. Due to some uncertainty of the calculations at temperatures around 400 K, the rate constant was approximated in the present work by simple Arrhenius expression listed in Table 1 with estimated uncertainty factor of 2.

The rate constant of reaction
$HOCO+O_2=HO_2+CO_2$ (40)
has been measured only at room temperature [40-42]. Poggi and Francisco [43] performed ab initio calculations and found calculated barrier of an adduct formation with eventual dissociation into products of 1.6 kcal/mol. Yu and Muckerman [44] extended these calculations using a direct dynamic method and calculated thermal rate constant from 200 to 1000 K. The value obtained at room temperature was in good agreement with available measurements. In the present work the results of Yu and Muckerman [44] were approximated by the non-Arrhenius expression shown in Table 3. The uncertainty factors of this reaction were evaluated as 2 taking into account experimental scattering and uncertainty of the modeling Yu and Muckerman [44].

No attempt to "adjust" the reaction rate coefficients was made in the present work; however, possible modifications within the uncertainty factors listed in Table 1 will be discussed below in connection with the analysis of the mechanism performance.

Updated mechanism

The detailed reaction mechanism used in this study is listed in Table 3. All reactions are reversible; in the modeling, the reverse rate constants are calculated from the forward rate constants and thermodynamic data by the Chemkin chemical interpreter code [45] and the one dimensional laminar code CHEM1D developed at Eindhoven University of Technology [46]. Thermodynamic data used are all from the latest database of Burcat and Ruscic [47]. In the following, the sources of the rate constants are shortly outlined. Also temperature range over which the rate constants were determined and associated uncertainty are presented. An estimated uncertainty factor, UF, implies that the rate constant is expected to be in the range k/UF < k < k*UF. All rate coefficients in the present work are given in cm^3 - mole - s units, while activation energies are in cal/mole.

Table 2: Reactions present in various CO submechanisms

Reaction	Yetter (1991)	Davis (2005)	Saxena (2006)	Li (2007)	Sun (2007)	Present work
$CO+O+M=CO_2+M$	+	+	-	+	+	+
$CO+O_2=CO_2+O$	+	+	+	+	+	+
$CO+OH=CO_2+H$	+	+	+	+	+	+
$CO+HO_2=CO_2+OH$	+	+	+	-	+	+
$HCO+M=H+CO+M$	+	+	+	+	+	+
$HCO+O_2=CO+HO_2$	+	+	+	+	+	+
$HCO+H=CO+H_2$	+	+	+	+	+	+
$HCO+O=CO+OH$	+	+	+	+	+	+
$HCO+O=CO_2+H$	-	+	+	+	+	+
$HCO+OH=CO+H_2O$	+	+	+	+	+	+
$HCO+HO_2=CO_2+OH+H$	-	-	-	+	+	+
$HCO+HCO=CH_2O+CO$	-	-	-	+	+	+
$HCO+HCO=H_2+CO+CO$	-	-	-	+	+	+
$HOCO(+M)=H+CO_2(+M)$	-	-	-	-	-	+
$HOCO+OH=H_2O+CO_2$	-	-	-	-	-	+
$HOCO+O_2=HO_2+CO_2$	-	-	-	-	-	+

Table3: H/O kinetic mechanism, units are cm^3 - mole - s - cal - K, $k = AT^n \exp(-E_a/RT)$. UF - uncertainty factor.

No	Reaction	A	n	E_a	Temperatures	UF	Source
1a	$H+H+M=H_2+M$ [a]	7.00E+17	-1.0	0	77 - 5000	2	[48] [d]
	Enhanced third-body efficiencies (relative to Ar):						
	$H_2 = 0$, $N_2 = 0$, $H = 0$, $H_2O = 14.3$				300 - 2000	5	[48] [d]
1b	$H+H+H_2=H_2+H_2$	1.00E+17	-0.6	0	50 - 5000	2.5	[48] [d]
1c	$H+H+N_2=H_2+N_2$	5.40E+18	-1.3	0	77 - 2000	3.2	[48] [d]
1d	$H+H+H=H_2+H$	3.20E+15	0	0	50 - 5000	3.2	[48] [d]
2	$O+O+M=O_2+M$ [a]	1.00E+17	-1.0	0	300 - 5000	2	[49] [d]
	Enhanced third-body efficiencies (relative to Ar):						
	$O = 28.8$, $O_2 = 8$, $NO = 2$, $N = 2$, $N_2 = 2$,					2	[50, 51] [d]
	$H_2O = 5$					3	[52] [e]
3	$O+H+M=OH+M$ [a]	6.75E+18	-1.0	0	2950-3700	3	[53] [f]
	Enhanced third-body efficiency:						
	$H_2O = 5$						[54] [e]
4	$H+OH+M=H_2O+M$	2.20E+22	-2.0	0	300-3000	2	[36]
	Enhanced third body efficiencies(relative to N_2)						
	$H_2O=6.4$, $Ar=0.38$						
5a	$H_2O+M=H+OH+M$ [a]	6.06E+27	-3.312	120770	300 - 3400	2	[55] [f]
	Enhanced third-body efficiencies (relative to Ar):						[55] [f]
	$H_2O = 0$, $H_2 = 3$, $N_2 = 2$, $O_2 = 1.5$						
5b	$H_2O+H_2O=H+OH+H_2O$	1.E+26	-2.44	120160	300 - 3400	2	[55] [f]
6a	$H+O_2(+M)=HO_2(+M)$ [a,b]	4.66E+12	0.44	0	300-2000	1.2	[56] [d,g]
	Low pressure limit:	5.70E+19	-1.4	0	300-2000		[56] [d,g]
	$F_{cent} = 0.5$						
	Enhanced third-body efficiencies (relative to N_2):						
	$Ar = 0$, $H_2O = 0$, $O_2 =0$, $H_2 = 1.5$, $He = 0.57$						[57] [d,g,f]
6b	$H+O_2(+Ar)=HO_2(+Ar)$ [b]	4.66E+12	0.44	0	300-2000	1.2	[56] [d,g]
	Low pressure limit:	7.43E+18	-1.2	0	300-2000		[56] [d,g]
	$F_{cent} = 0.5$						

6c	$H+O_2(+O_2)=HO_2(+O_2)$ [b]		4.66E+12	0.44	0	300-2000	1.2	[56] [d,g]
	Low pressure limit:		5.69E+18	-1.094	0	300-700	1.3	[57] [d,g,f]
	$F_{cent} = 0.5$							
6d	$H+O_2(+H_2O)=HO_2(+H_2O)$ [b]		9.06E+12	0.2	0	1050-1250	1.4	[58] [d,g,f]
	Low pressure limit:		3.67E+19	-1.0	0	1050-1250		[58] [d,g,f]
	$F_{cent} = 0.8$							
7a	$OH+OH(+M)=H_2O_2(+M)$ [a,b]		1E+14	-0.37	0	200 - 1500	2.5	[24]
	Low pressure limit:		2.38E+19	-0.8	0	250 - 1400	2.5	[16] [d]
	$F_{cent} = 0.5$							
	Enhanced third-body efficiency:							
	$H_2O = 0$							
7b	$OH+OH(+H_2O)=H_2O_2(+H_2O)$ [b]		1E+14	-0.37	0	200 - 1500	2.5	[24]
	Low pressure limit:		1.45E+18	0	0	300 - 400	2.5	[16, 59] [d]
	$F_{cent} = 0.5$							
8	$O+H_2=OH+H$		5.06E+04	2.67	6290	297 - 2495	1.3	[60] [d,f]
9	$H+O_2=OH+O$		2.06E+14	-0.097	15022	800 - 3500	1.5	[16] [d]
10	$H_2+OH=H_2O+H$		2.14E+08	1.52	3450.	300 - 2500	2	[16] [d]
11	$OH+OH=H_2O+O$		3.34E+04	2.42	-1930	250 - 2400	1.5	[16] [d]
12	$HO_2+O=OH+O_2$		1.63E+13	0	-445	220 - 400	1.2	[61] [d]
13	$H+HO_2=OH+OH$		1.90E+14	0	875	300-1000	2	[24]
14	$H+HO_2=H_2O+O$		1.45E+12	0	0	300	3	[16] [d]
15	$H+HO_2= H_2+O_2$		1.05E+14	0	2047	250-1000	2	[16] [d]
16	$H_2+O_2=OH+OH$		2.04E+12	0.44	69155	298-1000	3	[62] [g]
17	$HO_2+OH=H_2O+O_2$ [c]		2.89E+13	0	-500	250-2000	3	[16, 24] [d]
		+	9.27E+15	0	17500		3	[16] [d]
18a	$HO_2+HO_2=H_2O_2+O_2$ [c]		1.03E+14	0	11040	300-1250	2.5	[63] [f]
		+	1.94E+11	0	-1409		1.4	
18b	$HO_2+HO_2+M=H_2O_2+O_2+M$		6.84E+14	0	-1950	230-420	1.4	[64] [d]
19	$H_2O_2+H=HO_2+H_2$		1.70E+12	0	3755	300-1000	3	[16] [d]
20	$H_2O_2+H=H_2O+OH$		1.00E+13	0	3575	300-1000	2	[16] [d]
21	$H_2O_2+O=HO_2+OH$		9.55E+6	2	3970	300-2500	3	[33] [d]
22	$H_2O_2+OH=HO_2+H_2O$ [c]		2.00E+12	0	427	240-1700	2	[65] [f]

23	CO+O(+M)=CO_2(+M)	1.80E+10	0.0	2384	300-3000	2	[26]
	Low pressure limit:	1.55E+24	-2.79	4190	300 - 3000	2	[66]
	Enhanced third-body efficiencies (relative to N_2): H_2 = 2.5, H_2O = 12, CO = 1.9, CO_2 = 3.8, AR = 0.87						[13]
24	CO+OH = CO_2 +H	2.23E+05	1.90	-1160	800-3500		[13]
25	CO+OH(+M)=HOCO(+M)	1.20E+07	1.83	-236	300-2500		[70]
	LOW /7.20E+25 -3.85 1550. / F_{cent} = TROE /0.6 10. 100000./ Enhanced third-body efficiencies (relative to N_2): H_2 = 2.5, H_2O = 12, CO = 1.9, CO_2 = 3.8, Ar = 0.87						
26	CO+O_2=CO_2+O	2.50E+12	0.0	47800	300-2500		[49]
27	CO+HO_2=CO_2+OH	1.15E05	2.278	17545	300-2500		[18]
28	HCO+M=H+CO+M	4.80E+13	0.0	15760	300-2500		[59]
	H_2/2.5/ H_2O/6.2/ CO/1.875/ CO_2/3.75/ AR/1.0/ CH4/3.2/ CH3OH/7.5/						
29	HCO+H=CO+H_2	9.00E+13	0.0	0.0	298-2500		[16]
30	HCO+O=CO+OH	3.00E+13	0.0	0.0	300-2500		[16]
31	HCO+O=CO_2+H	3.00E+13	0.0	0.0	300-2500		[16]
32	HCO+OH=CO+H_2O	1.08E+14	0.0	0.0	298-2500		[16]
33	HCO+O_2=CO+HO_2	2.70E+10	0.68	-470.0	298-2500		[16]
34	HCO+HO_2=CO_2+OH+H	3.00E+13	0.0	0.0	300-2500	5	[33]
35	HCO+HO_2=CO+H_2O_2	3.00E+12	0.0	0.0	300-2500	5	[33]
36	HCO+HCO=CH_2O+CO	2.70E+13	0.0	0.0	295-820	2	[38]
37	HCO+HCO=H_2+ CO+CO	3.00E+12	0.0	0.0	300-1000	3	[33]
38	HOCO(+M)=H+CO_2(+M)	1.74E+12	0.307	32930	200-300		[69]
	LOW/ /	2.29E+26	-3.02	35070			
	Enhanced third-body efficiencies						

	(relative to N_2): Ar = 0, H_2O = 0, O_2 =0, H_2 = 1.5, He = 0.57						
39	$HOCO+OH=H_2O+CO_2$	1.60E+13	0	560	250-800	2	[39], see text [g]
40	$HOCO+O_2=HO_2+CO_2$	1.38E+10	0.842	160	250-1000	2	[44], see text [f,g]

a All other species have efficiencies equal to unity.

b The fall-off behavior of this reaction is expressed in the form as used by Baulch et al. (1992) and others.

c Rate constant is the sum of two expressions.

d Review

e Estimate

f Measurements

g Theoretical calculations

Validation tries using experimental data on ignition delays and burning velocities available in the literature and most relevant to gas-turbine conditions.

Modeling details

The in-house CHEM1D 1-D laminar code was also used for modeling the combustion process in determining the flame speed. CHEM1D solves a set of equations describing the conservation of mass, momentum, energy and chemical components for chemically reacting flows. It uses an exponential finite volume discretization in space and the non linear differential equations are solved with a fully implicit, modified Newton method. An adaptive gridding procedure is also implemented to increase accuracy in the flame front by placing almost 80% of the gridpoints in the area with the largest gradients. The input to this code are the conditions (pressure, temperature, mixture composition), thermodynamic and transport data and the chemical reaction mechanism.

Simulations were performed for a number of conditions in examining their predictability by comparison with recent experimental data and other kinetic mechanisms. Experimental data at higher pressure with lean combustion was available for H_2/CO combustion with O_2-He as oxidizer. He suppresses the thermo-diffusive instabilities at higher pressure. Although replacing N_2 in air with He does change the flame temperature and speed but not the fundamental chemistry.

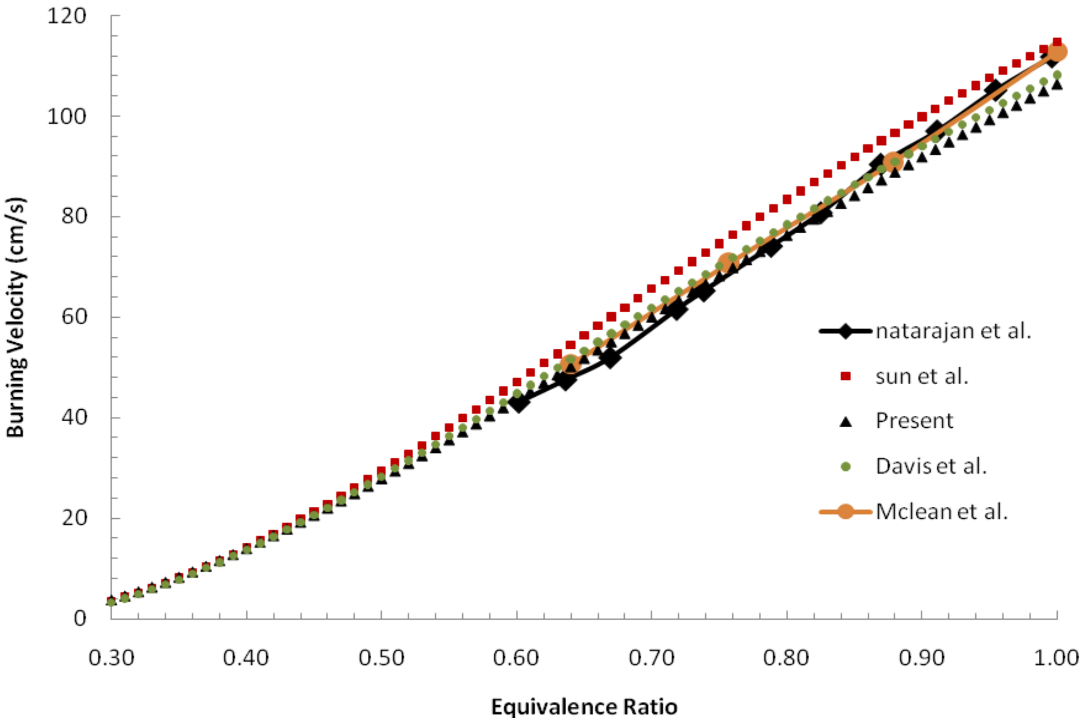

Fig 1. Laminar burning velocity of 50:50 H_2:CO fuel combusted in standard air at 1 atm and 300K.

Fig 1. Shows the variation of the burning velocity predicted by the present model for a H_2/CO (50:50) mixture with standard air over equivalence ratio from 0.3 to 1 at atmospheric pressure and 300K as initial temperature. The present model is in good agreement with recent experimental data [2]. Work of Mclean et al. [67] also produced experimental data for various mixtures of carbon monoxide and hydrogen and have been utilized by various researchers [13, 18] for model validation. When comparing for same parameters at higher preheat temperatures, Fig. 2 depicts over prediction by models. With increasing temperature there is an increase in over prediction.

However, present model tries to behave closer to the experimental data than the other recent models. Model proposed by Sun et al [18] overpredicts the most in all the three cases especially for lean mixtures. This model has been reported to be well in agreement with experiments for highly rich mixtures at high pressures(upto 40 bars).

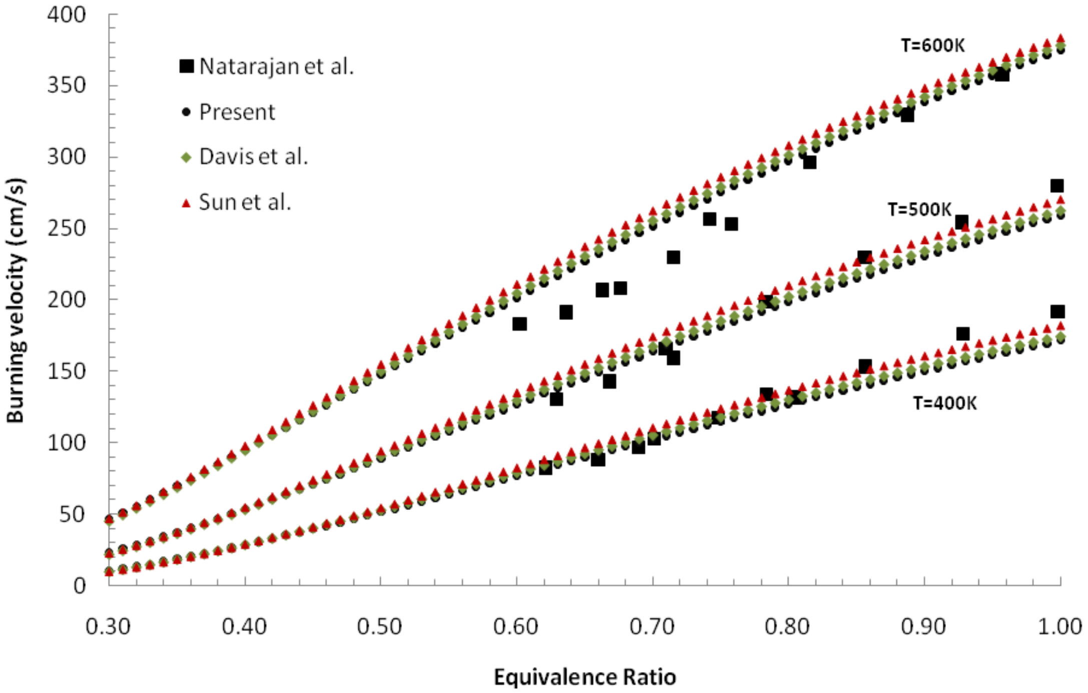

Fig 2. Laminar burning velocity of 50:50 H_2:CO fuel in standard air at atmospheric pressure and different preheat temperature

Fig. 3. Depicts the comparison of model predicted laminar burning velocity with experiments of Natarajan et al.[2]. 50:50 H_2:CO mixture was ignited in O_2:He(1:7 by volume) environment at 10 atm and 300K for a range of lean mixtures. This has also been identified as one of the deficiencies of the most recent models that over predict largely as the preheat temperature increases. An improvement suggested [2] is to revise the rate constants of the reactions

$$H+O_2+M=HO_2+M \qquad (6a)$$

$$H+HO_2=OH+OH \qquad (13)$$

$$CO+OH=H+CO_2 \qquad (24)$$

The second equation determines the destruction of HO_2 and is found to be sensitive (fig. 6). It is reponsible for heat release at the early part of the flame. The revision of this reaction rate constant will be in the future scope of this work.

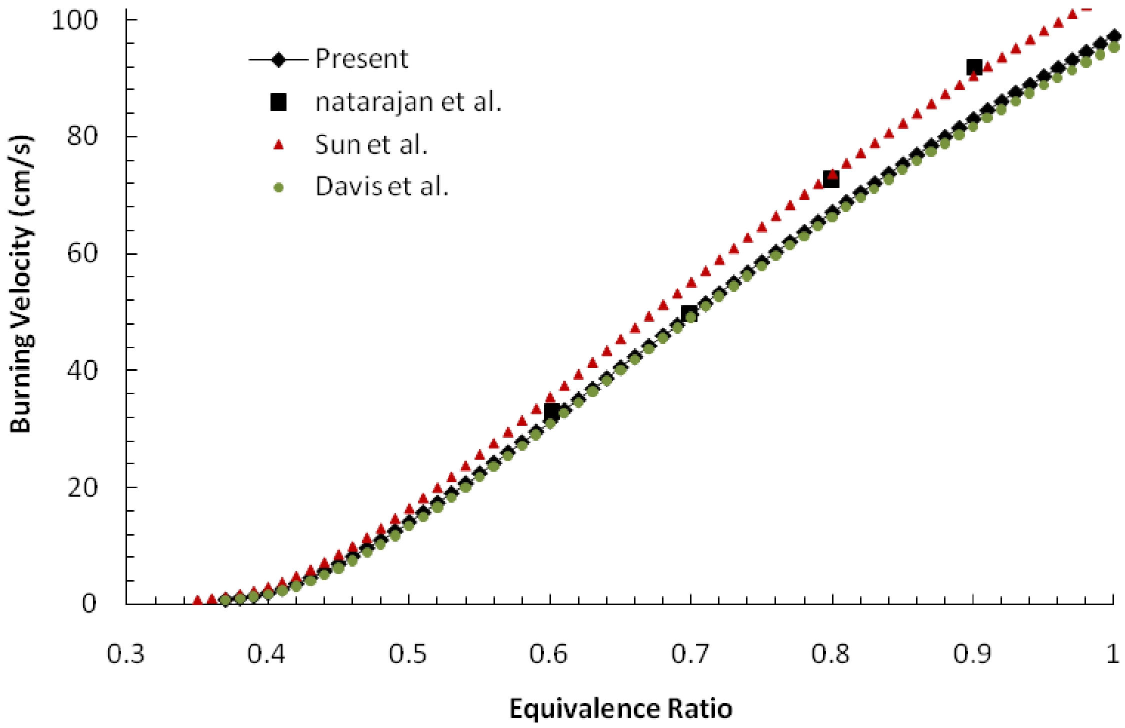

Fig. 3. Variation of laminar burning velocity with equivalence ratio at 10 atm and 300K. Square (symbol) shows the experimental data.

The variation of burning velocity with respect to different H_2:CO compositions at 2 atm and initial temperature 298K ignited in standard air has been shown in fig. 4.With lower content of H_2 (<5%), all the models almost conincide on a single line. This signifies the strength of the CO submechanism. This even exists at higher pressure and higher preheat temperature. However, with increasing H_2 content, the models deviate from each other emphasizing on the fact that H_2 submechanism has a lower strength in predicting accurate results. The recent model of Sun et al. [18] show greater increase in deviation from the present and Davis et al[10] model as the H_2 level increases as they have been reported suitable for rich mixtures and not necesaarily for lean mixtures.

To evaluate the behaviour of the reactions involved in the present mechanism at elevated pressures and initial temperatures, sensitivity analysis was performed at (1)stoichiometric T=300K and (2) Equivalence ratio 0.6 and 1 atm for a 50:50 H_2:CO mixture. Reactions with reasonable high sensitivity coefficients have been shown in the Fig. 5 and 6. Reaction (24) is very sensitive especially to higher pressure and tempearture which is also suggested in the literature. This reaction is the main door to the conversion of CO to CO_2 and also major fraction of energy release as this reaction occurs in the beginning (ignition) when OH reactions are more dominant [13]. Also, CO_2 concentration is important in determining adiabatic flame temperature as a function of pressure. The reaction occurs with internediate formation of HOCO and hence is pressure dependent [31]. Hence, a wise choice of rate constant for this reaction is quite important. Previous researchers have performed detailed calculations ot model the temperature and pressure dependence of this reaction[35, 31,13]. Li et al. [13] took into consideration a no. of parameters to fit experimental measured rate constants in the literature into a representative correlation which also has been used in the present study.

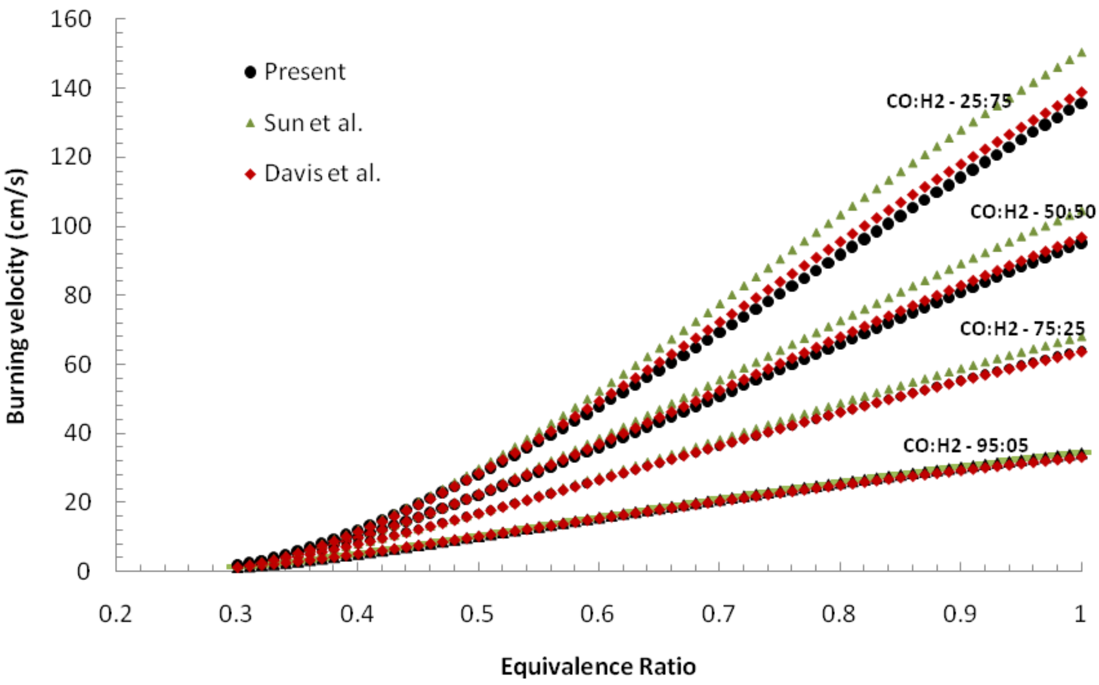

Fig. 4. Variation of laminar burning velocity with equivalence ratio for different CO:H_2 mixtures at 2 atm and 298K.

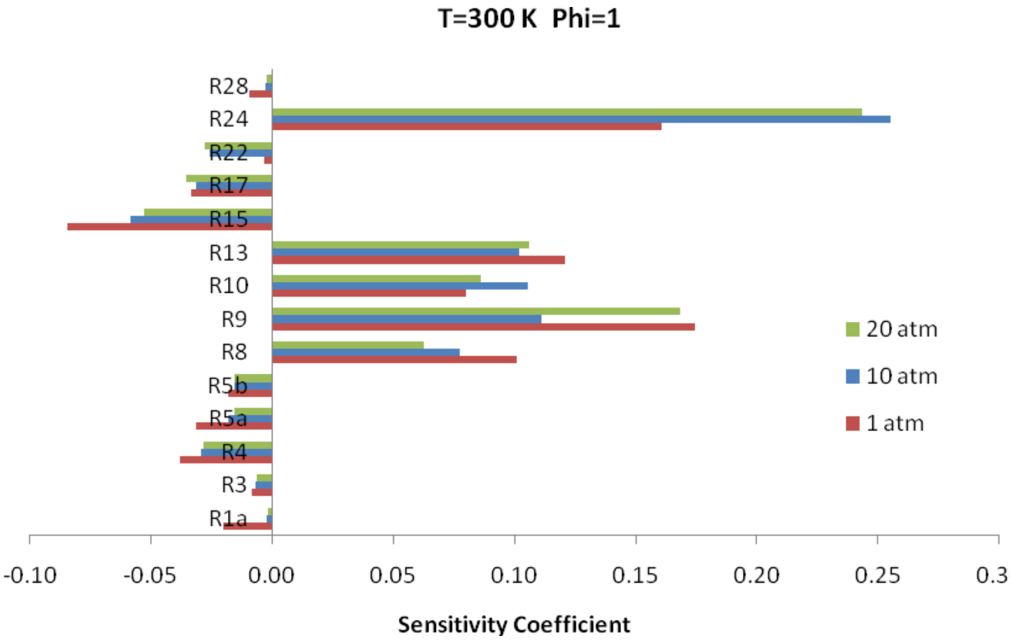

Fig. 5. Sensitivity coefficients of reactions of stoichiometric 50:50 H_2:CO mixtures at 300K at three different pressures.

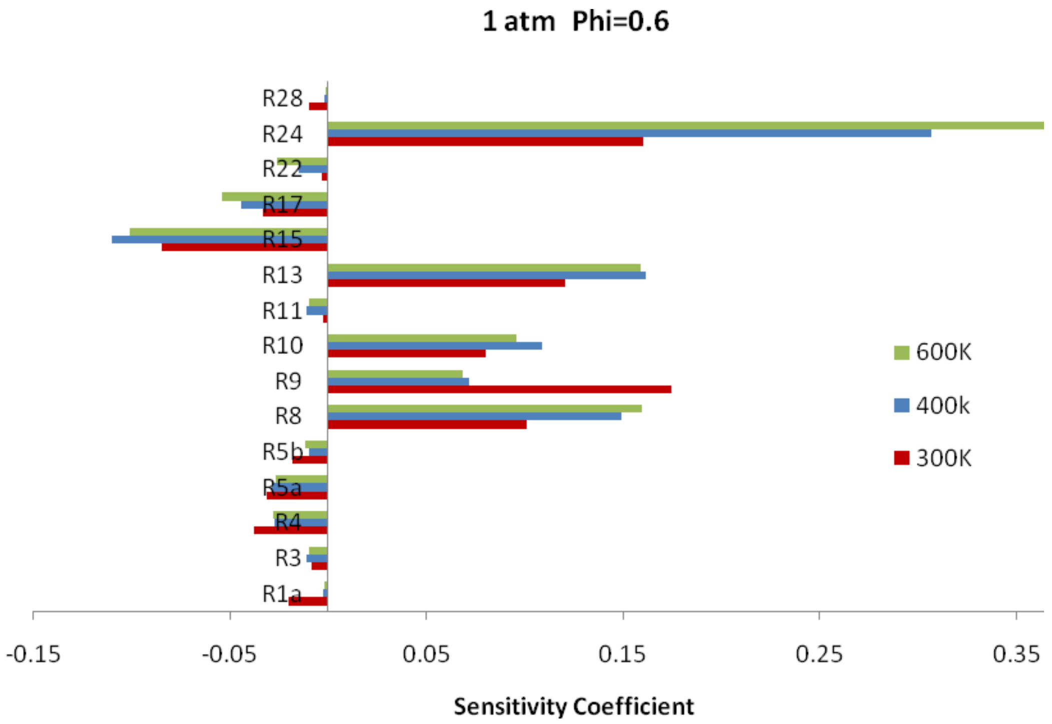

Fig. 6. Sensitivity coefficients of reactions of 50:50 H_2:CO mixtures at 1 atm at three different preheat temperatures.

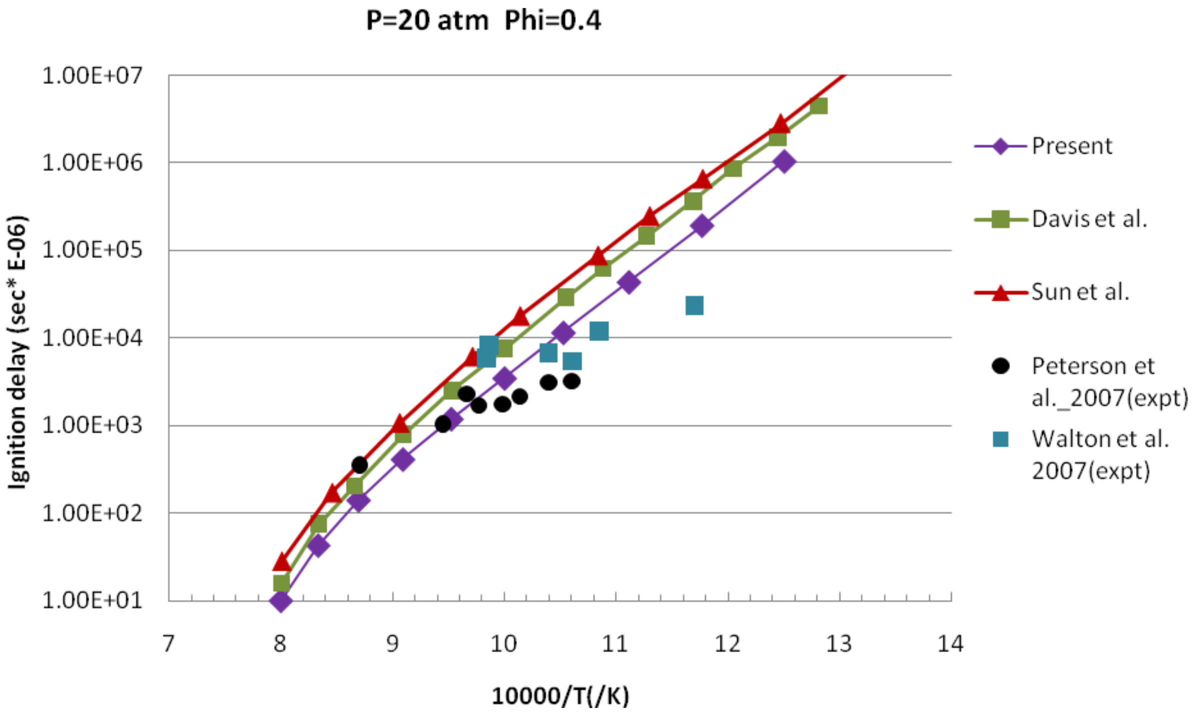

Fig. 7. Measured ([8] and [20]) and predicted ignition delay times of 50:50 H2:CO mixture at 20 atm.

Fig. 7 shows comparison of model predicted(lines) ignition delay times with experimental data available(points). The ignition delay time in the present study has been defined as the time when there is a temperature rise of 50K after the ignition. There are a number of definitions out of which rise in CO_2 concentration to a certain value defined for a particular mixture condition is the most popular in recent literature. The figure describes a 50:50 H_2:CO mixture ignited at 20 atm. For a temperature range from 900K and higher the model predictions match more or less with the experiments [20]. Mertens et al. [68] performed experiments at practical conditions of gas turbines for syngas at various compositions and determined the rate of the reaction (6a)

$$H+O_2(+M)=HO_2(+M) \qquad (6a)$$

The analysis [68] included shock tube experiments and was used to match the ignition time delay of modified kinetic mechanism of Davis et al. [10]. Present mechanism, however, uses rate constant suggested by Troe [56]. The above reaction will be one of the future scope in updating the present mechanism with more ignition delay data. Suggestions from Chaos et al. [23] has been taken into consideration in applying more accurate codes in determination of ignition delay from shock tube simulations.

CONCLUSIONS

Contemporary reaction mechanisms for H_{2-} -CO - O_2 system have been reviewed and evaluated. The list of reactions in these kinetic schemes is not always complete. New accurate measurements of the elementary reaction rates and updates in the thermodynamic data require its extensive validation. The contemporary choice of the reaction rate constants is presented with the emphasis on their uncertainties. Then the predictions of ignition, oxidation, flame burning velocities and flame structure of hydrogen - oxygen - inert mixtures are shown. Comparison of the modeling and experiments is discussed in terms of the range of applicability of the present mechanism.

Results of the calculations performed in this work using the H_2 submechanism [24] are in good quantitative agreement with the ignition experiments from 950 to 2700 K and from subatmospheric pressures up to 20 atm. The kinetic scheme has also been compared with the experimental data on hydrogen oxidation in the flow reactor at temperatures around 900 K. A general good agreement was found between the measurements at 0.3 and 1 atm and the simulation results. At higher pressures (15.7 atm) the experimental hydrogen concentrations are reproduced fairly well in the stoichiometric, lean mixtures and high pressure. The updated mechanism show good agreement with experiments for lean H_2/CO mixtures at higher pressure. With a number of simulations performed over lean mixtures (0.3 to 1) for preheat temperatures ranging from 298K to 600K , pressure from atmospheric to 20 atm and various H_2/CO compositions the mechanism gives reasonable results. The mechanism however has scopes of improvement in terms of determining burning velocities for higher pressure (upto 30 atm).

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