ON THE PREDICTABILITY OF CHEMICAL KINETIC MECHANISMS FOR THE DESCRIPTION COMBUSTION OF GASEOUS FUELS

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Abstract. *This work presents a systematic comparison between several detailed chemical kinetic models recently developed and available experimental data. The aim is to assess the predictive capabilities of the combustion with air of the following fuels: hydrogen, natural gas (methane), synthetic gas (Syngas) and liquefied petroleum gas (LPG), in a large range of equivalence ratio. The prevailing thermodynamical conditions range from ambient to the more stringent ones, such as high pressure combustion. In order to assess the predictive performance of the eight chosen chemical kinetics models, the results of numerical simulations are compared with existing experimental data of the combustion process in two simplified physical systems: the perfectly stirred reactor and the freely propagating premixed laminar flame. When ambient conditions are considered, the comparisons reveal a good agreement among most of detailed kinetic mechanisms on the prediction of thermochemical properties of practical interest with respect to the corresponding experimental data only, as far as lighter fuels such as hydrogen, methane and Syngas are considered. The chosen mechanisms are shown to meet with difficulties when mixtures of liquefied petroleum gas and air are considered, even in ambient conditions. The obtained results highlight the necessity for (i) updating the existing mechanisms with the use of recent experimental results and (ii) the development of new comprehensive models.*

Keywords: *Detailed kinetic mechanisms; Hydrogen; Natural gas; Syngas; Liquefied petroleum gas*

1. INTRODUCTION

In the past few years, the detailed chemical kinetic modeling has become one of the most important tools used in the description of the combustion process. The continuing development of detailed kinetic mechanisms for the combustion of several gaseous fuels was principally fomented by the necessity to satisfy more stringent criteria, such as the development of more efficient combustion systems and the reduction of the pollutant emissions in response to the expected depletion of the fossil fuels and the fulfillment of the environmental regulations. These energetic and environmental concerns convey the imperative need to understand of the combustion process as a fundamental step in order to utilize it in an efficient and environmental friendly way.

Because of the severest in national and international demands concerning to the environmental protection, special attention is being devoted to (i) the development of kinetic mechanisms for fossil fuels having rightly coupled the nitrogen kinetic scheme with the purpose of getting a complete understanding of the formation of NOx emissions, (ii) the development of new mechanisms for the combustion description of alternative fuels in order to to obtain a comprehension of the combustion phenomena, and their effects when alternative fuels are substituted by conventional ones. So, the validation of a specific kinetic mechanism for several conditions must be performed trough exhaustive comparisons of the simulation results obtained of simplified combustion systems against the corresponding experimental data.

Several detailed kinetic mechanisms for practical fuels can be found in the literature. For the case of simpler species, such as hydrogen and methane, there is not a complete neither unified kinetic scheme that can model the oxidation of these fuels in a broad range of operation conditions (pressure, temperature and equivalence ratio). When heavier hydrocarbons (i.e. butanes, heptanes, etc.) and/or mixtures of hydrocarbons (i.e. natural gas, liquefied petroleum gas, etc) are considered, the validation range becomes smaller. This difficulty appears as a consequence of the large number of degrees of freedom and the multiple reaction pathways that a kinetic mechanism must have for a complete description in the combustion of a specific fuel, particularly for lower temperature range in which, the chemical kinetic mechanisms are less studied. Currently, it is recognized that there is not a kinetic mechanism sufficiently complete or "comprehensive", even if for simple fuels such as hydrogen and methane. Thus, the use of existing combustion mechanisms requires, a priori, the knowledge of the corresponding validation range (Law *et al.*, 2003).

This paper aims to assess through comparison with recent experimental data, the predictive capabilities of available detailed kinetic mechanisms in the oxidation of the hydrogen, natural gas (methane), synthetic gas (Syngas) and liquefied petroleum gas (LPG). So, this paper begins with a brief bibliographical revision of the

most recognized detailed chemical kinetic mechanisms developed for the four aforementioned fuels. Then, the kinetic mechanisms considered are simulated and compared with recent experimental data available in the literature in order to choose the mechanisms that are the most suited to describe the combustion of each gaseous fuel at several operating parameters, particularly, at high pressure conditions.

2. BRIEF DETAILED MECHANISMS BIBLIOGRAPHY FOR GASEOUS FUELS

In a combustion process, the oxidation of a fuel is achieved by means of a substantial number of elementary reactions that describe the collision process among molecules. This ensemble of elementary reactions with the corresponding kinetic parameters define a combustion mechanism, also known as detailed kinetic mechanism. In this section, are briefly described several detailed kinetic mechanisms developed in the latest ten years by research groups worldwide, the majority of which are currently available for their evaluation and/or simulation in combustion systems.

2.1 Hydrogen Mechanism Description

The combustion of fossil fuels produces gases that are responsible for the greenhouse effect, and given the growing concern of the depletion of petroleum-base fuels resources, it is imperative to consider alternative fuels as energy source. Under this context, hydrogen is the most attractive alternative fuel because the combustion products are free of carbon dioxide, the main responsible for the greenhouse effect.

Although the oxidation process of this clean fuel involves two chemical elements (H and O) only, the kinetic description is of relative difficulty, since it involves several reaction steps that describe the initialization, propagation, branching and termination processes.

The development of chemical kinetic mechanisms for the hydrogen oxidation began with the work of Westbrook and Dryer (1981), which reported a revision of the chemical kinetic of combustion process, indicating that the H_2/O_2 mechanism is well characterized for a variety of numerical applications at atmospheric conditions.

In the 90's, Yetter et $al.$ (1991) published a detailed kinetic mechanism which consisted of 19 elementary reactions involving 9 chemical species in the H_2/CO oxidation. This mechanism was validated by Westbrook and Yetter (1993) through Plug Flow Reactor (PFR) experiments at $852 - 1138$ K and atmospheric pressure. The mechanism of Yetter et $al.$ (1991), was subsequently validated through shock tube experiments at $823 - 2870$ K, $0.3 - 2.2$ atm and $0.00005 - 3$ of equivalence ratio. Kim et $al.$ (1994) updated and validated the Yetter et $al.$ (1991) mechanism in PFR experiments for $1 - 9.6$ atm, $960 - 1200$ K and $0.33 - 2.1$ of equivalence ratio.

Mueller et $al.$ (1999) updated the Kim et $al.$ (1994) mechanism in which, simulations of PFR at $0.3 - 15.7$ atm and $850 - 1040$ K were conducted for the oxidation of 1 % of hydrogen with 0.5 % of oxygen in order to validate it. The experiments of Tse et $al.$ (2000) corresponding to spherical heat bomb at higher pressures, demonstrated the insufficiency of the Mueller et $al.$ (1999) mechanism for the hydrogen/air combustion in laminar flame predictions above 5 atm.

Afterwards, O'Conaire et $al.$ (2004) updated the Mueller et $al.$ (1999) mechanism and proposed a H_2/O_2 mechanism that consists of 21 chemical reactions and 9 elementary species. This mechanism has been validated against shock tubes experiments at $967 - 2700$ K and $1 - 87$ atm and laminar flame measurements of $H_2/O_2/N_2$ and $H_2/O_2/He$ at $1 - 20$ atm, 298 K and $0.5 - 5.5$ of equivalence ratio.

Li et $al.$ (2004) proposed a comprehensive H_2/O_2 mechanism which consists of 9 species and 19 chemical reactions and was built on the basis of the Mueller et $al.$ (1999) mechanism. The validation of the Li et $al.$ (2004) mechanism involves laminar flame experiments for $H_2/O_2/N_2$, $H_2/O_2/He$ and $H_2/O_2/Ar$ at $1 - 20$ atm, 298 K and within the flammability limits, and shock tubes experiments at $1 - 87$ atm and $900 - 2700$ K.

Konnov (2008) reported a recent modification of a previous version (Konnov, 2004) for the description of the hydrogen oxidation by updating of almost all the 30 kinetic rates in accord to recent chemical data, particularly, those reported by Baulch et $al.$ (2005). This mechanism is capable to describe shock tube experiments at $900 - 2700$ K and pressures that range from the atmospheric to 87 atm. The Konnov (2008) mechanism was also validated through laminar flame experiments at $0.35 - 4$ atm and at ambient temperature.

2.2 Natural Gas Mechanism Description

The development of the detailed chemical kinetic mechanism for the natural gas combustion began in the 70s, when several high-temperature kinetic models for the hydrogen, carbon monoxide and methane oxidation were constructed under the support of large quantity of experimental data (Seery and Bowman, 1970; Cooke and Williams, 1971). During the early 80s, the first chemical mechanism for combustion of the C1 and $C2$ hydrocarbons was proposed, being composed of 93 reversible elementary reactions and 26 chemical species (Westbrook et $al.$, 1982). This mechanism was subsequently revised by Westbrook and Dryer (1984) by the

addition of elementary reactions for *C*1 and *C*2 sub-mechanisms. These authors also suggested the addition of *C*3 elementary reactions in order to get an accurate numerical description of the methane combustion.

The compilations of Glarborg *et al.* (1986) and Miller and Bowman (1989) were the starting point of the development of the nitrogen oxidation mechanisms. Years later, Baulch et al. (1992) and Baulch et al. (1994) as representative members of the Group of Evaluation of Kinetic Data of the *Commission of European Communities*, CEC, published two compilations concerning the updated rate coefficients for many elementary reactions relevant to the oxidation of simple fuels. These compilations were newly updated and expanded (Baulch *et al.*, 2005) on the basis of recent theoretical and experimental studies of elementary reactions.

Frenklach *et al.* (1992) proposed a set of systematic procedures which combustion researches should account in order to develop a "comprehensive" chemical kinetic mechanism for any fuel. These recommendations were followed during the construction of the most popular kinetic models, such as the GRI (Smith *et al.*, 1999) and Leeds (Hughes *et al.*, 2002) mechanisms.

The development of the GRI mechanism started in 1995 by the *Gas Research Institute* in order to describe the methane oxidation (Frenklach *et al.*, 1995a). It is based on a set of elementary reactions, where the attributed values for the reaction rate parameters are provided trough the association of theoretical, experimental, and numerical data. The early versions of the GRI-Mech were the GRI-Mech 1.1 (Frenklach *et al.*, 1995a) and the GRI-Mech 1.2 (Frenklach *et al.*, 1995b). The GRI-Mech 3.0 (Smith *et al.*, 1999) is the latest version currently available, which was built for the combustion of the natural gas and considers 37 chemical species and 325 reversible elementary reactions.

The GRI-Mech 3.0 presents many advantages and drawbacks; the most relevant advantage is the good representation of the majority of experimental results available for the natural gas combustion, as well as the most relevant constituents hydrocarbons, methane and ethane. However, this is only verified when application conditions are close to laboratory conditions. The absence of "hierarchy" is the main drawback of the GRI-Mech that leads to the inability of shifting new kinetic parameters without retuning when accurate experimental data becomes available (Hughes *et al.*, 2002), and the awkwardness in developing new mechanisms for other heavier hydrocarbons using the GRI-Mech as a building block.

The Leeds mechanism is devoted to the modeling of the higher gaseous fuels, such methane, ethane, ethylene, acetylene, carbon monoxide and hydrogen, in a broad range of operational parameters. This mechanism was built in a same way as the GRI-Mech, namely, by means of the utilization of gas kinetics measures, although the former was developed accounting for the reference of kinetic data published by Baulch *et al.* (1992) and Baulch *et al.* (1994). The current version available is the 1.5 (Hughes *et al.*, 2002), which consists of 351 irreversible reactions and 37 chemical species, when the NOx oxidation is not considered. The Leeds Methane, NOx and SOx mechanism (Hughes *et al.*, 2002) accounts for the nitrogen and sulfur oxidation kinetics and includes 78 species and 892 irreversible (450 reversible) reactions.

The Konnov kinetic mechanism is another mechanism that simulates the natural gas combustion, as well as the *C*2 − *C*3 hydrocarbons combustion, the hydrogen oxidation and the NOx formation in flames. This mechanism was developed on the basis of the methane mechanism developed by Borisov *et al.* (1982), where important extensions were considered, such as the methanol and ethanol mechanisms (Borisov *et al.*, 1992a; Borisov *et al.*, 1992b), the NOx mechanism from Miller and Bowman (1989) and the CEC compilations kinetic data (Baulch *et al.*, 1992; Baulch *et al.*, 1994). The last version, the Konnov 0.5 mechanism (2000), was recently reviewed in 2007, and includes 127 chemical species and 1200 reversible elementary reactions.

Another kinetic model for the natural gas combustion was elaborated by the *Center for Energy Research* of the *University of California* at San Diego. The San Diego mechanism is based on the principle that a kinetic mechanism must only include a moderate number of species and reactions that are representative of the description of several fuels as methane, methanol, ethane, ethylene, ethanol, propane and propyne. The San Diego 20051201 (2005) is the last version available and considers 180 reversible reactions and 40 chemical species.

Researches from the CNRS (*Centre National de la Recherche Scientifique*), with the support of the *Gaz de France* developed a chemical kinetic mechanism for the combustion *C*1 − *C*3 hydrocarbons, GDF-Kin (Tan *et al.*, 1994). This mechanism has a hierarchical structure, i.e., it was sequentially developed starting from the hydrogen oxidation mechanism up to the heaviest hydrocarbons sub-mechanism available. The first version of the GDF-Kin mechanism consists of 508 reversible elementary reactions involving 82 chemical species (Tan *et al.*, 1994). An upgrade was proposed by El Bakali *et al.* (2006), which consists of the revision of the GDF-Kin 2.0 (El Bakali *et al.*, 2004) with the addition of the kinetics of nitrogen oxidation from Dagaut *et al.* (1998) NOx sub-mechanism. The number of elementary reactions and chemical species of the GDF-Kin 3.0 reaches 883 and 121, respectively.

Le Cong and Dagaut (2007) developed a kinetic mechanism initially consisting of 737 reversible reactions and 98 chemical species, which allows to simulate the natural gas and Syngas combustion over an extensive

range of operation conditions. This mechanism was built upon the mechanism developed by Dagaut (2002) for the combustion of the natural gas, and the systems used in the validation of this mechanism include shock tubes, premixed laminar flames, PSRs and PFRs. Recently, Le Cong and Dagaut (2008) extended their previous mechanism (Le Cong and Dagaut, 2007) in order to describe the combustion of mixtures of hydrogen and natural gas diluted on water vapor. This last version contains 128 chemical species involving 924 elementary reversible reaction. Excellent agreements were found between of this mechanism and several existing experimental data (Le Cong, 2007).

2.3 Synthetic Gas Mechanism Description

The use of Synthetic Gas (Syngas) as a fuel is motivated by the development of installations of Integrated Gasification Combined Cycle (IGCC), which generates electricity through utilization of the biomass or coal as fuel.

The oxidation kinetic of the Syngas has been studied widely at the beginning of the 80's and several works were conducted to determinate the elementary reaction rates for the kinetic of hydrogen and carbon monoxide mixtures in order to get a complete understanding of the combustion process of this fuel.

In the 90's several kinetic mechanism for the Syngas combustion were proposed and consecutively validated for a variety of thermodynamic conditions. Yetter $et\ al.$ (1991) proposed a detailed chemical mechanism for the $H_2 - CO$ oxidation that was the building block in the development of more sophisticated mechanisms for the Syngas combustion. Mueller $et\ al.$ (1999b) extended their previous H_2 mechanism (Mueller $et\ al.$, 1999a) by the addition of the CO oxidation. This extended mechanism was the basis of the development of the Davis $et\ al.$ (2005) mechanism, which includes of 16 chemical species and 30 elementary reactions.

Sun $et\ al.$ (2007) proposed a kinetic mechanism for the H_2/CO oxidation which consisted of 33 elementary reactions and 13 chemical species. This mechanism was constructed under updated kinetic rate compilations (Baulch $et\ al.$, 2005: Troe $et\ al.$, 1998, etc.) and was validated against experiments of laminar flame at ambient temperature, the oxidation at of 5% : 95% - 50% : 50% of $H_2 : O_2$ diluted in He for pressures within 1-40 atm.

Le Cong (2007) conducted an extensive study devoted to the validation of a kinetic mechanism for the description of the Syngas combustion in which 11 species and 26 reactions were included, and was considered as a subset of the Le Cong and Dagaut (2008) mechanism for the description of the natural gas combustion, already cited in the previous section.

Recently, Natarajan $et\ al.$ (2009) simulated the GRI 3.0 and the Davis $et\ al.$ (2005) mechanisms in order to evaluate their performance in the prediction of the laminar flame velocity in the oxidation, at atmospheric pressure, of 50% : 50% and 5% : 95% of H_2/CO for temperatures ranging from 300 to 700 K and at at lean equivalence ratio $(0.6-1)$. The comparison of both mechanisms against Bunsen flame measurements evidences a good agreement of both mechanisms in the laminar flame velocity predictions or temperatures within 300 - 500 K. However, a poor performance in the prediction of the experiments is evidenced as, simultaneously, the temperature increases above 500 K and the equivalence ratio goes up to the stoichiometry.

2.4 Liquefied Petroleum Gas Mechanism Description

The Liquefied Petroleum Gas (LPG) is extensively utilized as an alternative fuel in internal combustion engines as well as a domestic fuel. It is mainly formed by propane and butane, however, other heavier hydrocarbons, such pentane and hexane may be present in a variety of proportions. This fuel is produced commercially in refine industries and is stored at high pressures and temperatures that are below of the critical temperature, in order to maintain it at liquid phase.

The principal advantage of the LPG, when is compared to gaseous fuel of industrial use (i.e., natural gas), consists on the ease of liquification and storage in pressurized vessels, consequently, its transportation is allowed by the use of tanks and cylinders. Furthermore, the LPG has a good "interchangeability" property, defined as the ability of a fuel to substitute another one in a combustion process without significatively altering the performance, in terms of efficiency and pollutant emissions.

The development of detailed chemical mechanism for the LPG oxidation began at the end of XX century with the publications of Warth $et\ al.$ (1998) and Sung $et\ al.$ (1998), that reported the construction of detailed kinetic mechanims for the n-butane oxidation.

The kinetic scheme of Warth $et\ al.$ (1998) involves 778 reactions and 168 chemical species, whereas the Sung $et\ al.$ (1998) mechanism comprehends a set of 92 species including 621 elementary reactions. This last mechanism was validated by Sung $et\ al.$ (2001), via comparisons of Davis and Law (1998) experiments. It was proven the accuracy of this mechanims on the prediction of laminar flame velocity in the iso-butane and n-butane combustion with air at standard contidions of pressure and temperature.

The experimental work of Mishra and Rahman (2003) determined, by the use of a constant volume combus-

tion chamber, the flammability limits of air and LPG (30% of butane and 70% of propane) at ambient conditions and within $0.53-2.48$ of equivalence ratio. Furthermore, Dagaut and Hadj Ali (2003) built a detailed mechanism that consists of 827 reactions involving the kinetic of 112 chemical species. This mechanism was developed having as a basis the natural gas mechanisms of Dagaut (2002) and Dagaut et al. (2000), and the iso-butane mechanism of Dagaut et al. (1994).

The validation of the Dagaut and Hadj Ali (2003) kinetics was made using Jet Stirred Reactor (JSR) experiments at atmospheric pressure and for temperatures within the 950 and 1450 K in the combustion of a mixture of 24.8% of iso-butane, 39% of propane and 36.2% of propane as being characteristic of a LPG. This mechanism was also validated through experiments of laminar flames by Liao et al. (2004), which determined, by experiment and simulation, the laminar flame velocity of a LPG mixture composed by 0.02% of ethane, 0.92% of propylene, 27.65% of propane, 1.72% of butilene, 25.68% of iso-butane and 42.6% of n-butane at ambient conditions and $0.7-1.4$ of equivalence ratio.

A detailed kinetic mechanism was developed by a group at the *University of Southern California* (USC) in order to describe the $C1-C4$ combustion (Wang et al., 2007). This mechanism was built over the Davis et al. (2005) mechanism for the H_2/CO oxidation, with de addition of the GRI 1.2 (Frenklach et al., 1995b) and GRI 3.0 (Smith et al., 1999) mechanisms for the description $C1-C2$ hydrocarbons, and by the inclusion of the sub-mechanism $C3$ of Davis et al. (1999) propene combustion mechanism. The 2.0 is the last version available of the USC mechanism (Wang et al., 2007), which consists of 111 species involving 784 reversible reactions. With the exception of the premixed laminar flame simulation of pure hydrocarbons including the propane and n-butane at ambient conditions, there is not, to the best of the authors' knowledge, a work that validates the last version of this mechanism for the combustion of LPG.

3. METHODOLOGY

Since many relevant combustion devices operate at pressures above ambient, this paper reports the validation of eight recent kinetic mechanisms available for the combustion of the hydrogen, natural gas (methane), synthetic gas (Syngas) and liquefied petroleum gas (LPG), against experimental data available in the literature, in a broad range of thermodynamical conditions that range from ambient to more stringent ones.

In order to analyze the performance of several kinetic mechanisms for the aforementioned gaseous fuels, recent experimental data corresponding to the determination of the laminar flame velocity and the prediction of major and minor species evolution in a Jet Stirred Reactor (JSR) operation are considered. Although it is also possible to compare mechanism predictions against other experimental data, such counter flow diffusion flames and constant volume shock tubes, these simulations are not considered for sake of brevity.

Unstrained one-dimensional laminar flame velocity calculations are performed using the PREMIX (Kee et al., 1986) computer code within the CHEMKIN program (Kee et al., 1989) in order to validate the several kinetic mechanisms in premixed laminar flames situations. The converged solution is obtained considering a distribution of adapted grid points and accounting for the gradient and curvature criteria to be 0.1. The PSR code (Glarborg et al., 1991) of the CHEMKIN program is used to determine the thermochemical properties in the operation of a Jet Stirred Reactor (JSR), for this case, species concentrations are calculated from the balance among the net rate of production of each species and the balance between the input and output flow rate of these species.

In the case of the hydrogen oxidation, are considered the Li et al. (2004), the O'Conaire et al. (2004), the Konnov (2008) mechanisms and the GRI 3.0 (Smith et al., 1999) mechanisms, whereas San Diego 20051201 (2005), the GRI 3.0 (Smith et al., 1999) and the Le Cong and Dagaut (2008) mechanisms are used for the comparisons concerning of the methane combustion. The Davis et al. (2005) and the USC 2.0 (Wang et al., 2007) mechanisms are considered, respectively, for the Syngas and LPG combustion.

4. RESULTS AND DISCUSSIONS

In this section, the comparison of the obtained results with the eight aforementioned detailed kinetic mechanism is presented against recent experimental data available at the literature for the combustion of the hydrogen, natural gas (methane), Syngas and liquefied petroleum gas.

4.1 Hydrogen Oxidation Mechanisms

The laminar flame velocity of hydrogen and air has been experimentally measured at different values of pressure and equivalence ratio (Dowdy et al., 1990; Aung et al.. 1998; Tse et al., 2000). Measurements of a hydrogen/air premixed laminar flame velocity at moderate pressures (over 10 atm) are rare to find due to the limitations imposed by thermo-diffusive instabilities arising and as a consequence of the high Reynolds
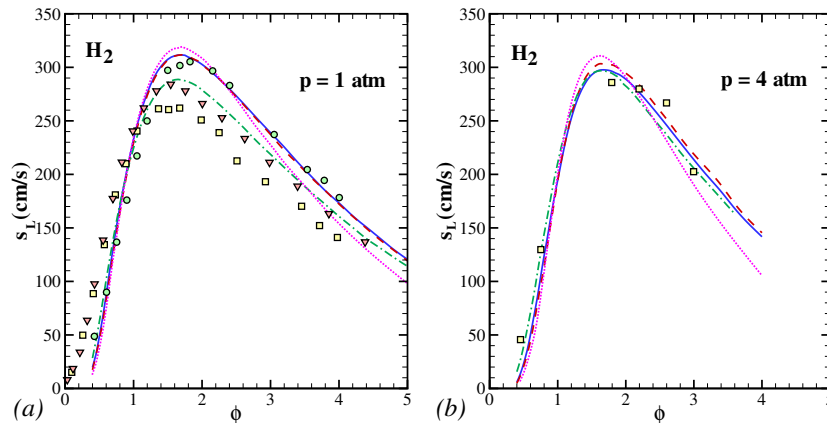
number at such pressures (Tse *et al.*, 2000).

Figure 1. Comparisons among the simulated (lines) and calculated (dots) of the premixed laminar flame velocity in the oxidation of the hydrogen with air for (a) 1 atm. and, (b) 4 atm. — Li *et al.* (2004); −− O'Conaire *et al.* (2004); −·− Konnov, (2008); · · · GRI 3.0 (Smith *et al.*, 1999); □ Aung *et al.*, (1998); ○ Tse *et al.* (2000); and ∇ Dowdly, *et al.* (1990).

Fig. 1a depicts a comparison at atmospheric conditions (1 atm and 280 K) of the laminar flame velocity calculated by the use of the Li *et al.* (2004), O'Conaire *et al.* (2004), Konnov (2008) and GRI 3.0 (Smith *et al.*, 1999) mechanisms, against the experimental data from Dowdy *et al.* (1990), Aung *et al.* (1998) and Tse *et al.* (2000). An important dispersion is observed by the most recent experiments, even at atmospheric conditions, of the laminar flame velocity, which maximum values range from 260 to 310 cm/s. Moreover, an excellent accord is obtained from the Li *et al.* (2004) and O'Conaire *et al.* (2004) mechanisms against the experimental data developed by Tse in all equivalence ratio range. The Konnov (2008) mechanism reproduces accurately the Tse *et al.* (2000) experiments only at lean mixtures, but it yields a good representation of the Dowdy *et al.* (1990) data in the rich equivalence ratio region. The GRI 3.0 mechanism predicts a maximum laminar flame velocity of 320 cm/s at $\phi = 1.7$, slightly superior than that obtained by the experimental results. When the equivalence ratio is increased, the the GRI 3.0 predictions underestimate the Tse *et al.* (2000) and Dowdy *et al.* (1990) data. None of the mechanisms analyzed in this work reproduce the Aung *et al.* (1998) experiments in all the rich region of equivalence ratio.

Fig. 1b shows the laminar flame velocity of the hydrogen/air combustion at ambient temperature and 4 atm. This figure allows to verify that the Konnov (2008) mechanism offers a good representation of most of the measurements performed by the Aung *et al.* (1998) data, whereas the Li *et al.* (2004) and O'Conaire *et al.* (2004) mechanisms predict values that are slightly lower and higher in the lean and rich regions, respectively.
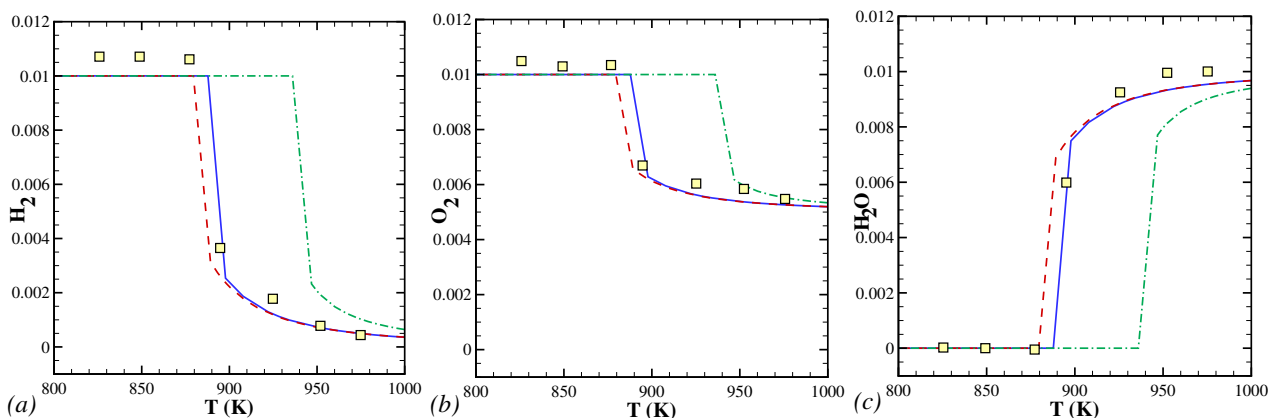

Figure 2. Comparisons among the simulated data (lines) using several mechanisms with respect to experimental data of Le Cong and Dagaut (2009) about the combustion of 1 % of H_2 with O_2 diluted on N_2, in the operation of a JSR for 1 atm of pressure, 0.5 of equivalence ratio and $\tau_r = 120$ ms. — Li *et al.* (2004); −− O'Conaire *et al.* (2004); −·− GRI 3.0 (Smith *et al.*, 1999); and □ Le Cong and Dagaut (2009).

The Li *et al.* (2004), O'Conaire *et al.* (2004), and the GRI 3.0 mechanisms are also used to simulate a situation

similar to the experimental data of Le Cong e Dagaut (2009), corresponding to the Jet Stirred Reactor (JSR) operation for 1% of hydrogen and oxygen (ϕ = 0.5) diluted with nitrogen at ambient pressure and 800 − 1000 K. As can be seen at Fig. 2, the evolution of the major species at the exit of a JSR reported by Le Cong and Dagaut (2009) is better predicted by the Li *et al.* (2004) and O'Conaire *et al.* (2004) mechanisms than by the GRI 3.0 mechanism. This last mechanism estimates 940 K for the combustion extinction, in contrast with the Li *et al.* (2004) and O'Conaire *et al.* (2004) mechanisms, which estimate a combustion extinction near to 890 K, similar to the experimental results from Le Cong and Dagaut *et al.* (2009).

4.2 Natural Gas Oxidation Mechanisms

The analysis of the combustion mechanism for the natural gas combustion is performed by the use of experimental data related to methane combustion. This usual procedure is justified by the large representativity of this alkane in the chemical kinetics description of the natural gas, and by the availability of a vast amount of experimental information related to the combustion kinetic of this hydrocarbon.
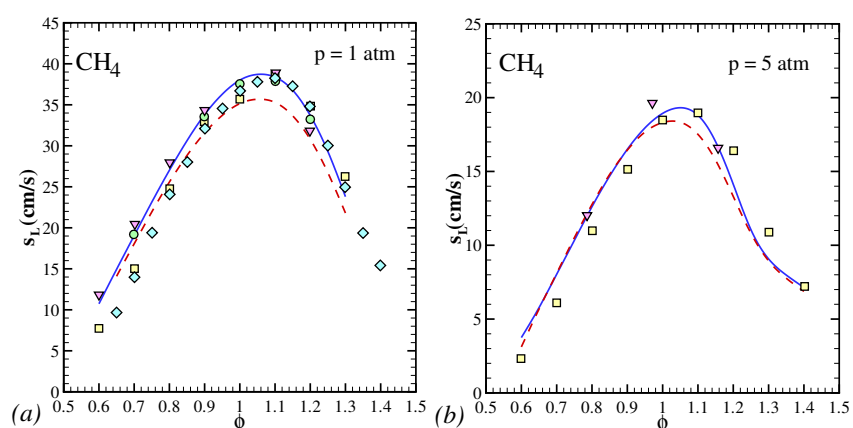

Figure 3. Comparisons among the simulated (lines) and calculated (dots) of the premixed laminar flame velocity in the oxidation of the methane with air for (a) 1 atm., and, (b) 5 atm. — GRI 3.0 (Smith *et al.*, 1999); −− San Diego 20051201, (2005); □ Rozenchan *et al.* (2002); ○ Ouimette and Seers, (2009); ∇ Gu *et al.* (2000); and ◇ van Maaren and de Goey (1994).

Fig. 3a presents the results obtained when using the GRI 3.0 (Smith, *et al.*, 1999) and San Diego 20051201 (2005) mechanisms and the experimental ones reported by Rozenchan *et al.* (2002), Ouimette and Seers (2009), Gu *et al.* (2000) and Van Maaren and de Goey (1994), related to a premixed laminar flame of methane and air at ambient conditions. It is important to mention the impossibility of obtaining laminar flame solutions, due to problems related to convergence, with the Konnov (2000) and Le Cong and Dagaut (2008) mechanisms. Fig. 3a shows that the GRI 3.0 exhibits a good agreement with the measurements of Ouimette and Seers (2009) and Gu *et al.* (2000) in all the equivalence ratio range, whereas the the San Diego 20051201 mechanism reproduces the experimental results the Rozenchan *et al.* (2002) and Van Maaren and de Goey (1994) only in the 0.8 and 1 region of equivalence ratio, underestimating the experiments at the rich mixing region. A comparison between the GRI 3.0 and the San Diego 20051201 mechanisms reveals a discrepancy in the laminar flame velocity that does not overcome the 15% for equivalence ratios from 0.95 to 1.15. However, this disagreement is reduced as the mixture moves to the lean or to the rich region.

For the sake of extending these comparisons, Fig. 3b shows the laminar flame velocity calculated by the GRI 3.0 and San Diego 20051201 mechanisms and compared to the experimental results of Rozenchan *et al.* (2002) and Gu *et al.* (2000) in the combustion of a premixed methane/air at 5 atm and ambient temperature. In this specific case, the GRI and San Diego mechanisms predict, with relative accuracy, the measurements of Rozenchan *et al.* (2002) and Gu *et al.* (2000) in all the equivalence ratio range (0.7 − 1.4), showing deviations that reach 10%. A comparison between the GRI and the San Diego mechanisms reveals similar disagreements of the laminar flame velocity at the vicinity of the stoichiometric region. However, the discrepancy does not overcome 7%, proving a good estimate in the prediction of s_L for both mechanism when the pressure is moderate.

The GRI 3.0 and San Diego 20051201 mechanisms have also been used to determine the velocity of a premixed laminar flame submitted to high pressures, and the corresponding results are shown in Fig. 4. Fig. 4a reveals an excellent agreement obtained from the use of both mechanisms against the majority of experimental data from Rozenchan *et al.* (2002) and Gu *et al.* (2000) at 300 K and 10 atm. However, as the pressure is increased to 20 atm, significant deviations are obtained in the s_L value by the use of the GRI mechanism with respect
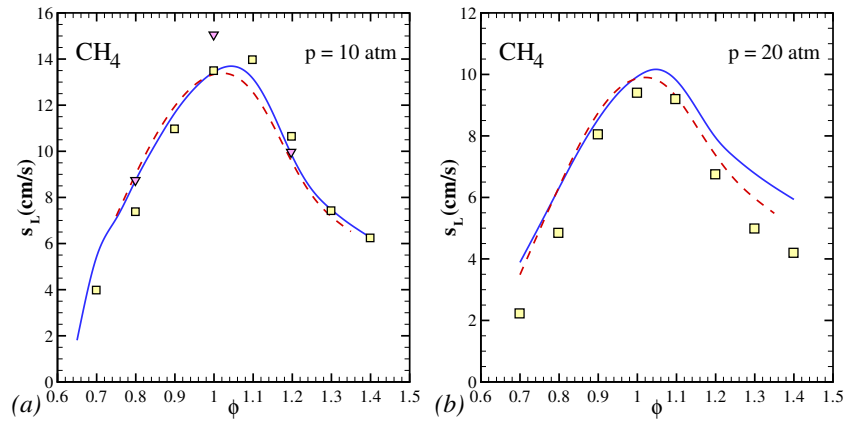
Figure 4. Comparisons among the simulated (lines) and calculated (dots) of the premixed laminar flame velocity in the oxidation of the methane with air for (a) 10 atm., and, (b) 20 atm. — GRI 3.0 (Smith *et al.*, 1999); −− San Diego 20051201, (2005); □ Rozenchan *et al.* (2002); and ∇ Gu *et al.* (2000).

to San Diego mechanism. This latter mechanism is the one which better predicts the Rozenchan *et al.* (2002) experiments, as can be verified in Fig. 4b.
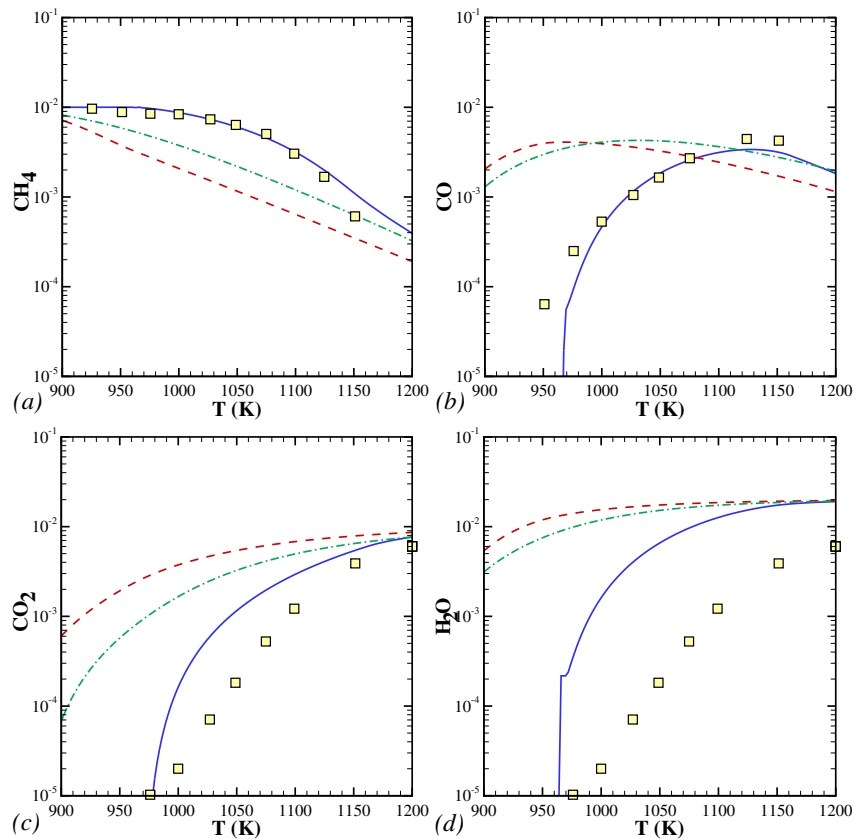

Figure 5. Comparisons a the simulated data (lines) using several mechanisms with respect to experimental data of Le Cong and Dagaut (2009) about the combustion of 1 % of H_2 with O_2 diluted on N_2, in the operation of a JSR for 1 atm of pressure, 0.5 of equivalence ratio and τ_r = 120 ms. — Le Cong and Dagaut (2008); −− GRI 3.0 (Smith *et al.*, 1999); −·− San Diego 20051201 (2005); and □ Le Cong and Dagaut (2007).

The experimental data from Le Cong and Dagaut (2007), corresponding to the Jet Stirred Reactor operation at high pressure has been modeled as a mean of comparing of the GRI 3.0 (Smith *et al.*, 1999), San Diego 20051201 (2005) and the Le Cong and Dagaut (2008) mechanisms.

Fig. 5 shows the evolution of the major species as a result of a combustion of 1% of methane with oxygen diluted in nitrogen, in a Jet Stirred Reactor at 10 atm and 120 ms of residence time, τ_r. In this

figure it can be noted the good estimative that the Le Cong and Dagaut (2008) mechanism provides when compared to the experimental measurements, whereas the GRI 3.0 and San Diego 20051201 mechanisms diverge considerably from the Le Cong and Dagaut (2007) experiments, underpredicting the reactants concentrations and overestimating from the combustion products formation.

The results underscore the inadequacy of GRI 3.0 and San Diego mechanisms to the prediction of the thermochemical parameters of the methane combustion in a PSR operating at higher pressures, in contrast to the Dagaut and Le Cong (2008) mechanism, that is well suited for this kind of simulation.

4.3 Synthetic Gas Oxidation Mechanism

Fig. 6 shows the results of laminar flame velocity obtained experimentally by Sun *et al.* (2007) and compared with the numerical simulation using the Davis *et al.* (2005) mechanism in the combustion of 25 % of hydrogen with 75 % of carbon monoxide diluted with Helium at 298 K and at high pressures. The computed results for this specific composition indicate that, for a pressure of 10 atm (Fig. 6a), an excellent agreement can be seen between the Davis *et al.* (2005) mechanism results in all the equivalence ratio range when is compared with the experimental results.
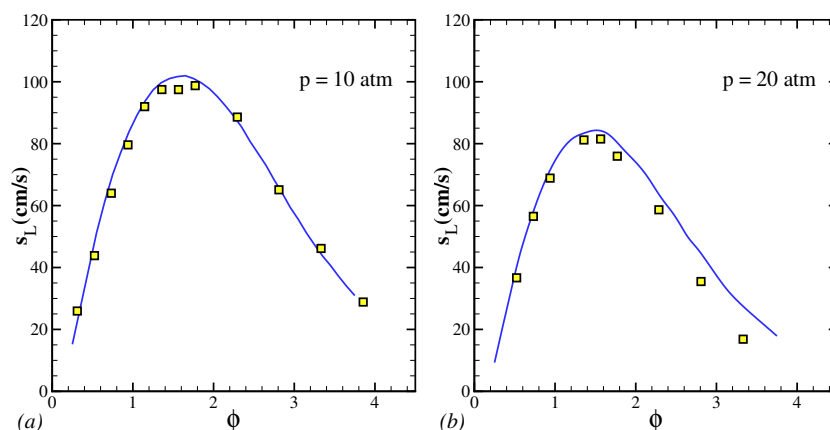

Figure 6. Comparisons of the Davis *et al.* (2005) mechanisms with the experiments of Sun *et al.* (2007) in the calculus of the laminar flame velocity for the oxidation of a characteristic Syngas (25 % of H_2 and 75 % of CO) diluted with Helium ($O_2 : He = 1 : 7$). — Davis *et al.* (2005); and □ Sun *et al.* (2007).

Accordingly, for 20 atm (Fig. 6b), the accuracy in the flame velocity predictions by the Davis *et al.* (2005) is restricted for mixtures of Syngas/O_2/He with equivalence ratio smaller than 1.5. However, Davis *et al.* (2005) simulations tend to overestimate s_L as soon the equivalence ratio is increased above 1.5, and discrepancies on the prediction of s_L overcome the 25% in the rich mixture region.

4.4 Liquefied Petroleum Gas Oxidation Mechanisms

The comparisons of spherical bomb experiments by Liao *et al.* (2005) and numeric simulations using the USC 2.0 (Wang *et al.*, 2007) and Sung *et al.* (1998) mechanisms refer to the laminar flame velocity of a characteristic LPG with air at ambient conditions are shown at Fig. 7. In this case, an excellent agreement in s_L is found by both kinetic schemes when compared with the experimental data of Liao *et al.* (2005). This excellent agreement is guaranteed by the Sung mechanism in almost whole equivalence ratio range, in wich, discrepancies with respect to the measured data do not overcome 10 %. The USC 2.0 (Wang *et al.*, 2007) underpredicts, up to 25 %, the Liao *et al.* (2005) experiments as the mixing composition moves away the stoichiometry and becomes richer in fuel.

Also, in Fig. 7, it can be noticed a difference related to the estimate of the maximum value of the laminar flame velocity for these mechanisms. The USC 2.0 mechanism (Wang *et al.*, 2007) predicts a maximum value of s_L to be equal to 39 cm/s at 1.05 of equivalence ratio, whereas the results obtained by the Sung *et al.*(1998) mechanism estimates a value of 42 cm/s for the maximum laminar flame velocity at 1.1 of equivalence ratio, which is the closest estimated to the Liao *et al.* (2005) experimental data (41.6 cm/s at $\phi = 1.1$).

In the same way, Fig. 8. displays the laminar flame velocity obtained through numerical simulation using the Sung *et al.* (1998) and USC 2.0 (Wang *et al.*, 2007) mechanisms, plotted against the experimental data of Huzayyin *et al.* (2008) for ambient temperature combustion of another representative composition of LPG with air at 1 and 4 atm. In both cases, it can be noted that a large difference exists among the USC 2.0 and Sung
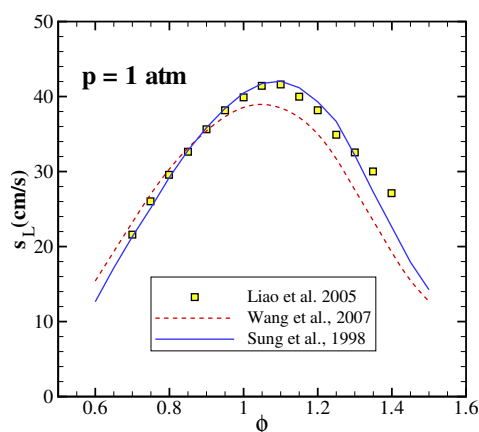
Figure 7. Comparisons of the results obtained with the USC 2.0 (Wang et al., 2007) and Sung et al. (1998) mechanisms against the Liao et al. (2005) experiments, in the determination of laminar flame velocity for the LPG combustion (0.02 % of C_2H_6, 0.92 % of C_3H_6, 27.65 % of C_3H_8, 1.72 % of C_4H_8, 25.68 % of i-C_4H_{10} and 42.6 % of n-C_4H_{10}) with air at ambient conditions. — Sung et al. (1998); −− USC 2.0 (Wang et al., 2007); and □ Liao et al. (2005).

mechanisms predictions against the Huzayyin *et al.* (2008) measurements. This marked difference indicates the necessity of further developments by both experimental and numerical approaches in relationship of that fuel. For the experimental case, it is evidenced the existence of a large dispersion in the laboratory data related to the laminar flame velocity for GLP mixtures. Another discrepant issue, that remains without explanation in the experimental work of Huzayyin *et al.* (2008), is the displacement of the maximum value of s_L near to 1.4 of equivalence ratio.
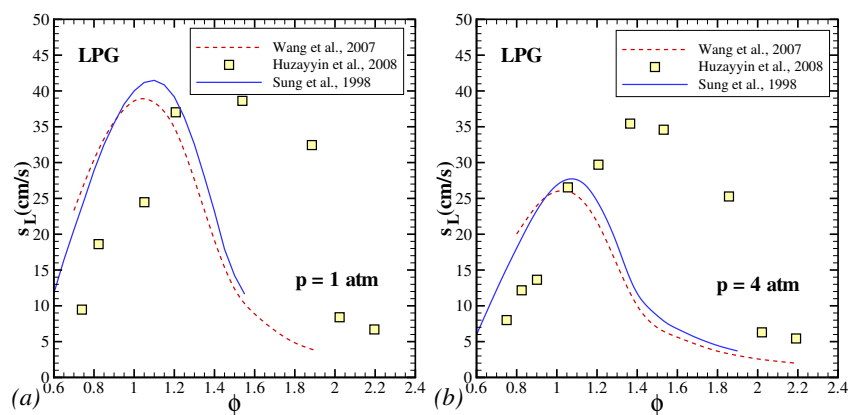

Figure 8. Comparisons of the USC 2.0 mechanisms against the Huzayyin data in the calculus of the laminar flame velocity for the combustion of a characteristic LPG consisting by 0.04 % of C_2H_6, 26.41 % of C_3H_8, 26.31 % of $i - C_4H_{10}$ and 47.22 % of $n - C_4H_{10}$. — Sung et al. (1998); −− USC 2.0 (Wang et al., 2007); and □ Huzayyin et al. (2008).

Fig. 9 depicts the CO, CO_2 and O_2 evolution calculated by the Le Cong and Dagaut (2008) and the USC 2.0 mechanisms in comparison with the corresponding experiment reported by the Dagaut and Had Ali (2003), for the combustion with air and another specific LPG (composed by 32.2 % of propane, 24.8 % of iso-butane and 39 % of n-butane) in a Jet Stirred Reactor at atmospheric pressure and for equivalence ratio 4.0. In this figure, one can observe a strong discrepancy between both the Le Cong and Dagaut (2008) and the USC 2.0 (2007) kinetic schemes when compared to the experiment.

The Le Cong and Dagaut (2008) mechanism reproduces tendencies similar to the Dagaut and Hadj Ali (2003) experiments, however these results correspond to an overprediction that are, in cases, 10 times the values reported in the experiment. On the other hand, the USC 2.0 mechanism exhibits a total inconsistency in the predictions with respect to the experimental data. This results exhibited by both mechanisms could be related to the lack of experimental data for the LPG combustion, allied to the difficulty in the development of comprehensive mechanisms for the LPG combustion due to the large number of species and reactions that demands a correct kinetic description.
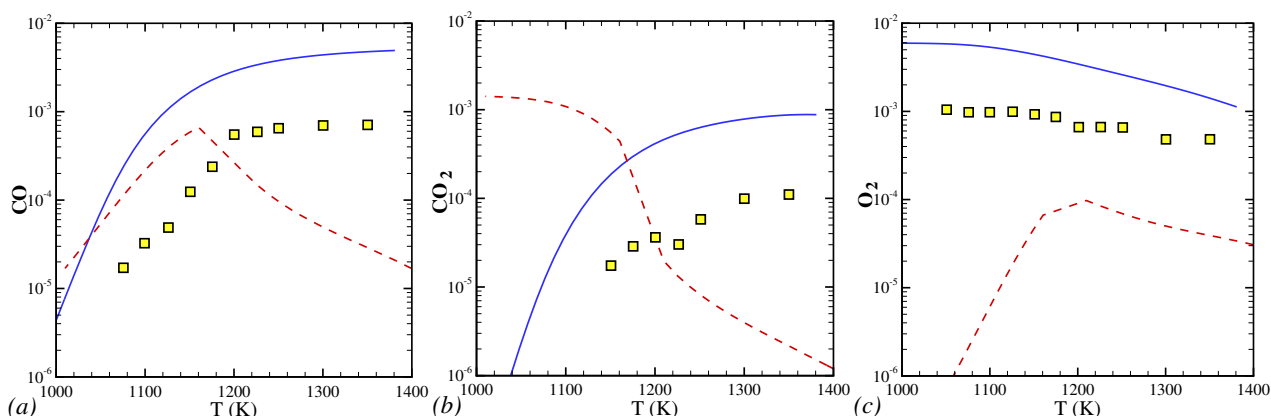
Figure 9. Comparisons a the simulated data (lines) using the USC 2.0 mechanism (2007) and Le Cong and Dagaut (2008) mechanisms with respect to experimental data (symbol) of Dagaut and Hadj Ali (2003) about the combustion of 1% of LPG (32.2 % of C_3H_8, 24.8 % of $i-C_4H_{10}$ and 39 % of $n-C_4H_{10}$), in the operation of a JSR for 1 atm of pressure, 4.0 of equivalence ratio and τ_r = 120 ms. — Le Cong and Dagaut (2008); −− USC 2.0 (2007); and □ Dagaut and Hadj Ali (2003).

5. CONCLUDING REMARKS

The present study presented a brief review of the principal unrestricted access detailed mechanism for the oxidation of gaseous fuels of practical interest. Some of these mechanisms were simulated and compared to recent experimental data, in order to characterize their performance, in two simplified combustion systems, i.e., the freely propagating premixed laminar flame and the Jet Stirred Reactor (JSR), in conditions ranging from atmospheric to the most stringent high pressure ones.

For the hydrogen oxidation, the results of the simulations indicate the Li *et al.* (2004) and O'Conaire *et al.* (2004) schemes are the mechanisms that better reproduced the set of recent experimental results. This conclusion is in agreement with those reported in similar works, i.e., Ströhle and Myhrvold (2006), which established that the Li *et al.* (2004) mechanism presented a better agreement in the prediction of the hydrogen oxidation over a broad operation conditions.

For the natural gas case, it was observed that a large predictability range is obtained when the GRI 3.0 (Smith *et al.*, 1999) mechanism was used in the laminar flame velocity calculations at atmospheric and moderate pressures. The San Diego 20051201 (2005) mechanism is the suitable one for the laminar flame simulations when the pressure is higher. In PSR simulations at elevated pressures, it was demonstrated the inadequacy in the use of the GRI 3.0 and San Diego 20051201 mechanisms, in contrast to the Le Cong and Dagaut (2008) mechanism, where the comparison between the modeling results and the experimental data suggested the accuracy of the latter as opposed to the formers.

Difficulties were encountered to access the Syngas kinetic schemes that consider the oxidation of the H_2/CO diluted with *He* for their validation at higher pressures. Only the The Davis *et al.* (2005) kinetics was available, and this mechanisms seems to be reliable in predicting the laminar flame velocity at high pressures. However, is important to stress the competence of the Sun *et al.* (2007) and Le Cong and Dagaut (2007) mechanisms in the simulation of the Syngas combustion in variety simplified systems and over a wide range of operation parameters.

In reference to the results obtained in this work, a good agreement was exhibited by the USC 2.0 (*Wang, et al.*, 2007) and Sung *et al.* (1998) mechanisms in the simulation of the combustion of the LPG in laminar flame at ambient conditions, whereas both mechanisms did not match the recent high and low pressure experimental data (Huzayyin *et al.*, 2008). When the operation of JSR is considered, the Le Cong and Dagaut (2008) mechanism provided more accurate representation than the USC 2.0 (2007) on the prediction of the evolution of majoritary species, although, the estimates reach 10 times those obtained in the experiments. So, the obtained results for the LPG combustion highlight the necessity for the updating the existing mechanisms with the use of recent experimental results as well as the development of new comprehensive kinetic models.

6. ACKNOWLEDGEMENTS

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