23rd ABCM International Congress of Mechanical Engineering
December 6-11, 2015, Rio de Janeiro, RJ, Brazil

ACCURACY AND COMPUTATIONAL EFFICIENCY STUDY OF REDUCED CHEMICAL KINETIC MECHANISMS FOR METHANE-AIR COMBUSTION

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Abstract. *Accurate predictions of minor chemical species and radicals are crucial for determining the production of pollutants such as soot. Reduced chemical kinetic mechanisms compromise their accuracy in favor of a lower computational cost. When using these reduced mechanisms then, it is important to asses both the accuracy of the results obtained, and the amount of computational time saved. This works describes such an assessment of seven reduced chemical kinetic mechanisms utilized for methane-air combustion. The reduced mechanisms evaluated involve different numbers of chemical species and reactions. The assessment is carried out using partially stirred reactors, with and without in situ adaptive tabulation-based chemistry acceleration techniques, by comparing the results with detailed chemical kinetics baseline computations. In terms of accuracy, the main results show that in general major species such as carbon dioxide are predicted reasonably well (~0.5-10% error) by the reduced mechanisms considered. Important differences between detailed and reduced mechanisms results (~5-65%) are observed however when predicting minor species such as acetylene. The in situ adaptive tabulation technique used in this work leads to further reductions in the accuracy of the minor species predicted, i.e., to further increases in prediction errors (~0-90%). Regarding the computational cost, the results show that savings of up to 80% can be obtained when using the reduced mechanisms analyzed. The use of chemistry acceleration techniques results in further cost reductions of about 40%. Overall the results obtained in this work emphasize the need of carefully selecting the reduced mechanism that is more suitable for a given application.*

Keywords*: Reduced chemical kinetic mechanisms, methane-air combustion, partially stirred reactors*

1. INTRODUCTION

Designing practical combustion systems that are both efficient and environmentally friendly requires an in-depth knowledge of the tight coupling between turbulent fluctuations, chemical reactions and mixing. One way of understanding turbulence-chemistry-mixing interactions involves the use of high fidelity modeling approaches, such as those based on probability density function (PDF) methods (Pope, 1985; Haworth, 2010). As it happens when using high fidelity models, the use of PDF-based approaches involves a high computational cost. The hybrid Euler/Lagrange schemes (Andrade *et al*., 2011; Celis and Figueira da Silva, 2015; Jenny *et al.*, 2001; Muradoglu *et al.*, 2003; Raman *et al.*, 2004; Raman *et al.*, 2005; Vedovoto *et al.*, 2015, Yang *et al.*, 2013) utilized for solving the PDF equations are mainly responsible for the high costs observed, as they require the use of a large number (millions) of Lagrangian notional particles. In this type of hybrid schemes, the Lagrangian part evolves the reactive scalars by advancing the particles in physical and composition spaces. This means that solving for a given Lagrangian particle implies integrating the chemical kinetic equations characterizing the chemical mechanism utilized for describing the combustion process. Even for a small hydrocarbon (methane), detailed chemical kinetic mechanisms describing its oxidation involve hundreds of chemical reactions and tens/hundreds of chemical species. Solving all detailed mechanisms chemical kinetics at each of the tens/hundreds of millions Lagrangian particles clearly implies a huge computational time. A need appears therefore for reduced chemical kinetic mechanisms, which are subject of the present work.

Starting from detailed chemical kinetic mechanisms, different methodologies can be utilized for deriving reduced mechanisms. These methodologies range from conventional ones, involving hypotheses about rate controlling reactions, for example, to more sophisticated ones, employing graph theory (Lu and Law, 2005) or computational singular perturbation-based methods (Goussis *et al.*, 1990; Lam, 1985; Lam, 1993; Massias *et al.*, 1999). Over the years thus, several reduced chemical kinetic mechanisms for methane-air combustion, with different complexity levels, have been derived. Early reduced kinetic mechanisms for methane oxidation typically consist of three to four steps (reactions). Examples of these kinetic mechanisms constitute those developed by Bilger *et al.*, (1990), Chen and Dibble (1991), Jones and Lindstedt (1988), Peters and Kee (1987) and Peters and Williams (1987). Although these early mechanisms proved to be valuable at the time of their development, their applicability range is quite limited, in terms of the

combustion phenomena described. Reduced mechanisms for methane-air combustion derived more recently typically involve a larger number of steps, i.e., 10-20 lumped reactions (Sung *et al.*, 1988; Sung *et al.*, 2001). These so-called augmented reduced mechanisms (ARMs) have been designed to be used in large scale simulations, and their applicability range is larger than that corresponding to earlier reduced mechanisms.

A reduced mechanism represents in general the minimum set of chemical reactions and species that reproduces, within a specified tolerance error, the initial detailed kinetic model. Using a reduced mechanism for a given numerical simulation implies then understanding both the level of inaccuracy incurred and the amount of computational time saved in the process. In addition, since reduced mechanisms are derived considering a particular set of operating conditions, their accuracy it is expected to vary when these conditions change. Accordingly, the main objective of this work is to assess, in terms of accuracy and computational time, different reduced mechanisms for methane-air combustion in a context similar to that found in transported PDF-based hybrid Euler/Lagrange approaches. This characterization is necessary before venturing in the modeling of the experimental configurations of interest to the authors (Caetano and Figueira da Silva, 2015). After this brief introduction (Section 1) thus, the reduced mechanisms considered here are described (Section 2). Section 3 deals with in turn the chemical reactor-based configuration utilized for assessing the different reduced mechanisms studied. The particular chemistry acceleration technique used for reducing computational time during simulations is also highlighted in this section. The final part of the paper (Sections 4 and 5) presents the results, in terms of accuracy and computational efficiency, associated with the reduced mechanisms analyzed here and the main conclusions (Section 6) drawn.

2. REDUCED CHEMICAL KINETIC MECHANISMS

Seven reduced chemical mechanisms for methane oxidation, listed in Table 1, have been evaluated in this work. The number of chemical species and reactions (steps) involved on each of these reduced mechanisms is given in Table 1. In addition this table indicates the GRI mechanism from where the reduced mechanisms were derived, the source from where they were obtained in Chemkin format and their corresponding references. The GRI mechanism used as reference when comparing the reduced mechanisms studied is the GRI-Mech 3.0 (GRI-Mech, 2014), denoted here as GM30. This detailed mechanism involves 53 chemical species and 325 reactions.

Table 1. Reduced chemical kinetic mechanisms studied.

Mechanism	Steps	Species	Based on	Source	Reference
CHEN5	5	9	GRI-Mech 2.11	User	Mallampalli *et al.*, 1998; Yilmaz, 2013
CHEN12	12	16	GRI-Mech 2.11	Sandia	Sandia, 2014; Sung *et al.*, 1998
ARM2	15	19	GRI-Mech 2.11	Sandia	Sandia, 2014; Cao and Pope, 2005
ARM12	12	16	GRI-Mech 3.0	Author	Sung, 2014; Sung *et al.*, 2001
ARM13	13	17	GRI-Mech 3.0	Sandia	Sandia, 2014
ARM15	15	19	GRI-Mech 3.0	Author	Sung, 2014; Sung *et al.*, 2001
ARM17	17	21	GRI-Mech 3.0	Author	Sung, 2014; Sung *et al.*, 2001

The smallest reduced mechanism analyzed here, denoted as CHEN5, corresponds to the 5-step mechanism derived by Mallampalli *et al.* (1998) for modeling the typical high pressure and fuel-lean conditions found in gas turbine combustors operating in lean premixed mode. CHEN12 is the GRI-Mech 2.11-based version of the GRI-Mech 1.2-based mechanism (Sung *et al.*, 1998), consisting of 16 species and 12 lumped reaction steps. The reduced mechanism giving rise to CHEN12 constitutes one of the first efforts made in order to develop a mechanism providing a more comprehensive description of combustion phenomena than those early mechanisms involving four- to five-steps only. The CHEN12 mechanism (also known as ARM1) has been successfully employed for performing transported PDF-based simulations of turbulent nonpremixed flames (Xu and Pope, 2000). The 15-step ARM2 (Cao and Pope, 2005) is the corresponding CHEN12 mechanism that includes NO (nitric oxide) chemistry. The reduced mechanisms ARM12, ARM15 and ARM17 (Sung *et al.*, 2001) constitute an extension of early efforts (Sung *et al.*, 1998) to include the latest GRI mechanism release, GRI-Mech 3.0, and the description of NOx (nitrogen oxides) formation. Finally, ARM13 is essentially the ARM12 mechanism without the H2 (hydrogen) oxidation involving the chemistry of HO2 (hydroperoxyl) and H2O2 (hydrogen peroxide), but including NO chemistry involving the chemical species NO, HCN (hydrogen cyanide) and NH3 (ammonia).

It is worth noticing that all reduced mechanisms considered here use *ad hoc* Chemkin compatible rate calculation routines for the computation of chemical species production rates. These routines have been provided by the mechanisms' developers along with the reduced mechanism in Chemkin format. The description of each of these rate routines associated with the reduced mechanisms is out of the scope of this work. The interested reader may follow the references given in Table 1 for the details of these routines, the description of the chemical species and reactions composing each of these reduced mechanisms, as well as the rationale behind the derivation of these reduced mechanisms.

3. CHEMICAL REACTOR-BASED CONFIGURATION

When applying transported PDF methods to turbulent combustion modeling, chemical reactions-related terms appear in closed form, which is a significant advantage when compared to classical presumed PDF approaches. Since there is an interest in using reduced kinetic mechanisms in transported PDF-based approaches, it is important to consider, for the assessment of these mechanisms, configurations representative of strong turbulence-chemistry interactions that may occur in practical combustion systems. Partially stirred reactors (PaSRs) (Orbegoso and Figueira da Silva, 2009; Sabel'nikov and Figueira da Silva, 2002) have been thus utilized for the assessment of the different reduced mechanisms studied in this work. These chemical reactors have been chosen because they present some of the basic features found in large scale PDF-based simulations. PaSRs allow for instance formulating PDF transport equations and using different mixing models.

The particular PaSR model used here allows both specifying fuel and oxidant as separate inlets and selecting different mixing and soot formation models. The PaSR-based code includes an *in situ* adaptive tabulation (ISAT) technique (Pope, 1997), which is used for reducing the amount of computer time required to treat chemistry in reactive flow calculations. The details of the specific ISAT scheme used in this work can be found in Cunha Jr and Figueira da Silva (2014). The PaSR-related routines along with the ISAT technique compose the so-called ISAT@PaSR platform used here for evaluating the reduced mechanisms.

In order to assess the performance of the reduced mechanisms, in terms of accuracy and computational time, several simulations using the ISAT@PaSR platform have been carried out in this work. The simulations are performed considering two inlet streams, one involving pure CH4 (methane) as fuel, and the other involving air as oxidant, both at 300 K and 1 atm. An atmosphere of pure CO2 (carbon dioxide), at 2100 K and 1 atm, is used as initial composition inside the PaSR. The interaction by exchange with the mean (IEM) model (Villermaux and Devillon, 1972), also known as the linear mean-square estimation (LMSE) model (Dopazo and O'Brien, 1974), is used as mixing model in all simulations carried out. A total number of particles (inside the PaSR) equal to 1024 is considered in the simulations, along a time step of 0.1 ms. Residence and mixing times are 2 and 0.2 ms, respectively. The total number of time steps simulated corresponded to 250 time steps (25 ms or 12.5 residence times).

Three different equivalences ratios, ϕ, obtained by changing the number of fuel particles entering the PaSR, i.e., 0.7, 1.1 and 1.5, have been studied. In this work all chemistry-related computations have been treated using Chemkin II routines (Kee *et al.*, 1991). More specifically, reaction processes are modeled using Arrhenius laws and integrated using DVODE (Byrne and Dean, 1993). When ISAT is used as a chemistry acceleration technique, an error tolerance of 10^{-3} is considered. Accordingly, several simulations of the reduced mechanisms summarized in Table 1 have been performed and their results have been compared with each other and with those associated with the detailed GRI-Mech 3.0 mechanism (GM30). The main outcomes from such comparisons are both described and discussed in the following two sections.

4. DIRECT INTEGRATION-BASED RESULTS

This section discusses results obtained by direct integration of the Arrhenius laws describing the chemical reaction processes only, i.e., without resorting to any chemistry acceleration technique.

4.1. Temporal evolution

Figure 1 illustrates the history, in terms of both means (top plots) and variances (bottom plots), of the reactor temperature and the OH (hydroxyl) and C2H2 (acetylene) mass fractions, according to the detailed mechanism GM30 and the seven reduced mechanisms studied. C2H2 is chosen for the analysis here due to its importance as a soot precursor. It is seen from this figure that, excepting the smallest reduced mechanism analyzed (CHEN5), all reduced mechanisms results follow the corresponding detailed mechanism. Accordingly, mechanisms ARM12 to ARM17 follow the GM30 detailed mechanism. This desired behavior is observed for both the means and the variances. The results obtained with the CHEN5 reduced mechanism can be considered as an exception. It is believed that the relatively small number of chemical species and reactions characterizing this mechanism is responsible for its particular behavior. Figure 1 highlights as well that each chemical species has its own fluctuation frequency, i.e., its own chemical time scale. When compared to C2H2 for instance, OH present a larger time scale. This finding implies in practice that OH takes less time steps than C2H2 to achieve a reactor steady state operation.

In addition, since the ARM mechanisms ARM12 to ARM17 closely follow the GM30, their level of accuracy is similar. Therefore, only the results corresponding to one of these ARM mechanisms, ARM17, are discussed here. Nevertheless, it is worth noticing that different computational times characterize each of the ARM mechanisms. In general, it has been observed that the computational time associated with the ARM12 to ARM17 mechanisms lie between those values corresponding to the CHEN12 and ARM17 mechanisms. Accordingly, henceforth, as detailed below, the analysis will restricted to the first three reduced mechanisms listed in Table 1, plus the ARM17 mechanism.

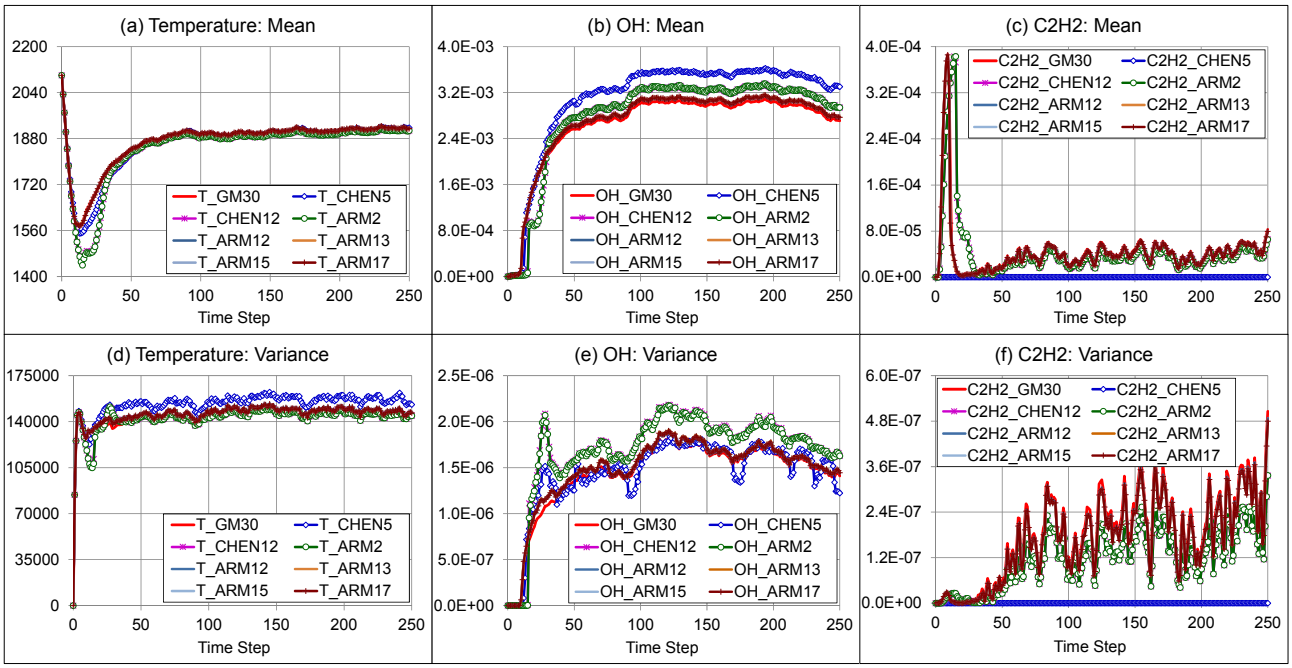

Figure 1. Temperature and OH and C2H2 mass fractions history (ϕ = 1.1) (top: mean, bottom: variance).

4.2. Mechanisms accuracy

The reduced mechanisms accuracy has been evaluated by analyzing steady state results of selected parameters characterizing the PaSR reactor operation. The end of the period simulated (time step 250) has been considered as the reactor steady sate condition. Parameters considered for the analyses include the reactor temperature and the mass fractions associated with both minor – OH, C2H2 and CO (carbon monoxide) – and major species – CH4 and O2. Accordingly, Figure 2 shows the relative differences (%) between the results associated with the GM30 detailed mechanism and those corresponding to each of the reduced mechanisms considered. There are several points to highlight in Figure 2. It is seen for instance that the reduced mechanisms accuracy varies with the equivalence ratio. Since reduced mechanisms are usually derived for a set of particular conditions, this result is not surprising. It is observed as well that the mechanisms accuracy increases with the increase in the size of the reduced mechanisms. In addition, Figure 2 illustrates that minor species accuracy suffer the most when decreasing the number of chemical species and reactions characterizing a reduced mechanism. Depending on the reduced mechanism application then, a mechanism size-related compromise needs to be achieved at some stage, so as to diminish the computer time involved, albeit preserving the prediction accuracy. Overall the results shown in Figure 2 provide the order of magnitude (up to 65%) of the errors incurred because of the use of reduced mechanisms featuring different levels of complexity.

4.3. Computational time

The mechanism size, i.e., the number of chemical species and reactions, controls the time required to complete a given number of simulation time steps. As it could have been expected thus, Figure 3a shows that the smallest reduced mechanism studied, CHEN5, presents the lowest computational cost. Notice that the total time, in absolute terms (seconds, s), shown in Figure 3a corresponds to, specifically, the time required to complete 250 time steps of a PaSR-based simulation processing 1024 particles per time step. Accordingly, as illustrated in Figure 3b, the total time required by a typical hybrid Euler/Lagrange scheme-based simulation, involving 15 thousand time steps and 100 million particles, would be of the order of hundreds of years (yrs). Even though parallel computing may reduce greatly these figures, these results emphasize both the large amount of computer time involved when performing transported PDF simulations, and the need of using chemistry acceleration techniques. Finally, using as reference the GM30 detailed mechanism, Figure 3c shows that reduced mechanisms may lead to savings in computer time of up to 80%, approximately. These large reductions in computational time are the main driving forces for the development and usage of reduced mechanisms in numerical simulations involving practical combustion systems.

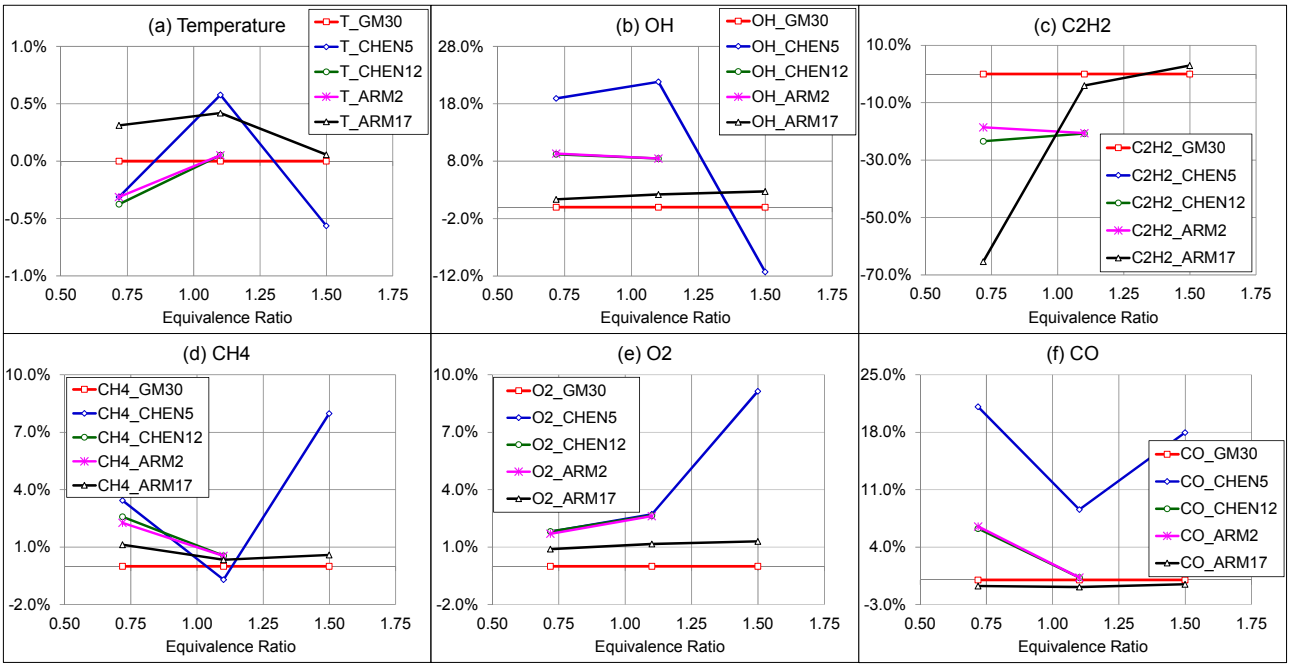

Figure 2. Reduced mechanisms accuracy (%), in terms of temperature and selected species mass fractions, as a function of equivalence ratio (reference values: GM30 detailed mechanism) – Direct Integration.

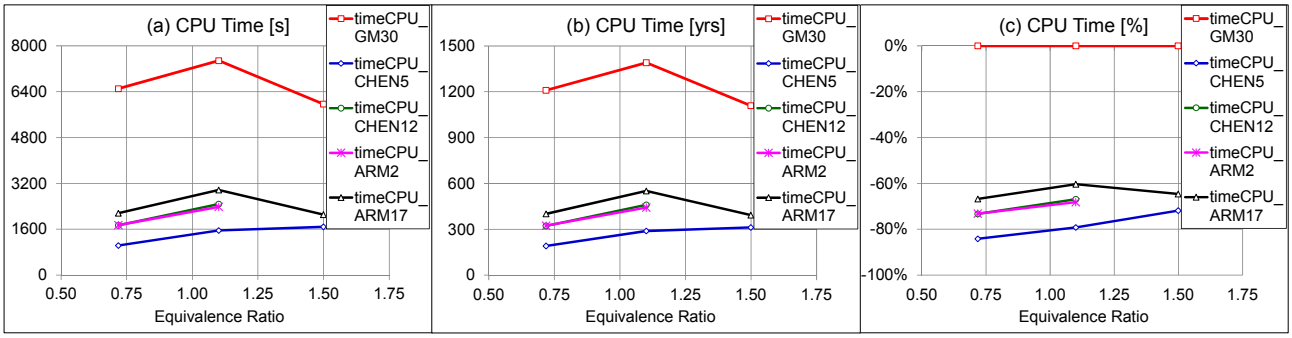

Figure 3. Reduced mechanisms computational efficiency – Direct integration.

5. CHEMISTRY ACELERATION TECHNIQUE-BASED RESULTS

The results discussed so far came from the application of direct integration processes only. In this Section 5, the corresponding results obtained by using an ISAT-based chemistry acceleration technique (Cunha Jr and Figueira da Silva, 2014) are discussed. When using an ISAT scheme, it may be useful (in transient conditions, for example) to recreate the ISAT binary trees. Nevertheless, a preliminary computer time-based analysis carried out in this work showed that, due to both the small number of time steps simulated and the particular reactor conditions considered, there is no need to perform binary three recreations. In addition, the referred analysis suggested avoiding the use of ISAT during the initial time steps of the reactor simulations carried out. Accordingly, the ISAT-related results presented here are obtained by using one binary tree only, which is initialized after time step 150.

5.1. Mechanisms accuracy

In order to allow a fair comparison of the reduced mechanisms analyzed when using ISAT, the relative results illustrated in Figure 4 are computed using as reference the corresponding direct integration ones. In other words, Figure 4 shows, for each mechanism, the relative differences (%) between the results obtained using direct integration only, and those obtained through the use of the ISAT-based technique utilized in this work. The parameters shown in this figure are identical to those in Figure 2. Figure 4 results suggest that, at least in terms of temperature and major species mass fractions, the ISAT usage accuracy errors are relatively small when compared to the use of the reduced mechanisms via direct integration (Figure 2). This finding is crucial as the amount of computational time saved when

using ISAT-related techniques is generally substantial. It is worth noticing as well that the accuracy reported in Figure 4 could be increased by reducing the ISAT error tolerance, which was kept equal to 10^{-3} in this work. Nevertheless, reducing this ISAT tolerance would bring penalties in the ISAT-related computational time savings. Once again, a compromise between accuracy and computational cost needs to be achieved at some stage.

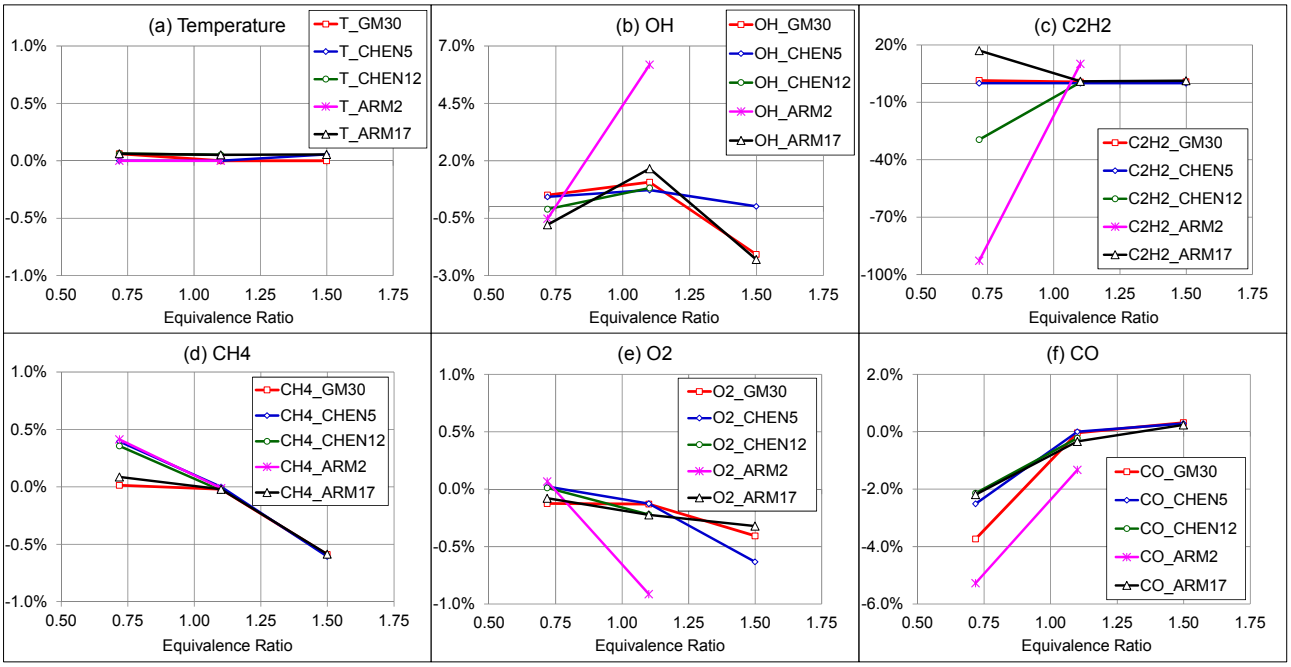

Figure 4. Reduced mechanisms accuracy (%), in terms of temperature and selected species mass fractions, as a function of equivalence ratio (reference values: direct integration-based results) – ISAT.

5.2. Computational time

Similar to what is presented in Figure 3 above, Figure 5a and Figure 5b show, respectively, the time required to complete 250 time steps in a PaSR-based simulation, and 15 thousand times steps in a typical hybrid Euler/Lagrange scheme-based simulation. When compared to the corresponding Figure 3a and Figure 3b above, the ISAT-related figures highlight the fact that the ISAT usage results in considerable computer time reductions. This finding can be better visualized in Figure 3c, which emphasizes the corresponding ISAT savings in computational cost. More specifically, Figure 3c indicates that the use of ISAT-based chemistry acceleration techniques may lead to costs reductions of about 40% when compared to those cases involving direct integration processes only. It is worth noticing as well that greater cost reductions are obtained for larger kinetic mechanisms. This is consistent with the typical scaling behavior of the ISAT tabulation and retrieval operations.

6. CONCLUSIONS

The high computational cost usually associated with computational fluid dynamics-based calculations precludes the use of detailed chemical kinetic mechanisms, which involve tens and even hundreds of chemical species and reactions, in numerical simulations of practical combustion systems. A compromise between accuracy and computational efficiency needs to be achieved then at some stage. In this work seven reduced chemical kinetic mechanisms utilized for methane-air combustion have been assessed. The reduced mechanisms evaluated involved different levels of complexity, in terms of numbers of chemical species and reactions. The assessment was carried out using partially stirred reactors, with and without ISAT-based chemistry acceleration techniques, by comparing the results obtained with those corresponding to detailed chemical kinetics baseline computations.

In terms of accuracy, the main results showed that in general major species such as carbon dioxide are predicted reasonably well (~0.5-10% error) by the reduced mechanisms considered. Nevertheless, important differences between detailed and reduced mechanisms results (~5-65%) were observed when predicting minor species such as acetylene. The ISAT technique used in this work led to further reductions in the accuracy of the minor species predicted, i.e., to further increases in prediction errors (~0-90%). Regarding the computational cost, the results showed that savings of up to 80% can be obtained when using the reduced mechanisms analyzed. The use of ISAT techniques resulted in further cost reductions of about 40%. From these results it is concluded that, even though they may lead to significant

reductions in computational time, both reduced kinetic mechanisms and chemistry acceleration techniques can greatly affect the accuracy of the results obtained. This is particularly true when minor species are accounted for. Overall the results obtained in this work emphasize the need of both (i) carefully selecting the reduced mechanism that is more suitable for a given application, and (ii) adequately setting the chemistry acceleration technique to be utilized in the simulation process. Further work will involve using the reduced mechanisms studied here in contexts involving hybrid Euler/Lagrange approaches allow modeling practical combustion systems.

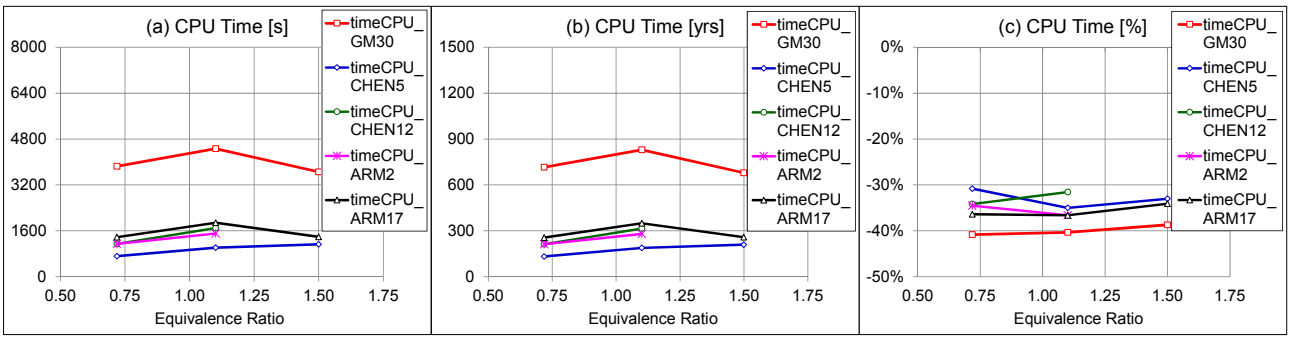

Figure 5. Reduced mechanisms computational efficiency – ISAT.

7. ACKNOWLEDGEMENTS

This work was supported by Petrobras under the technical monitoring of Dr. Ricardo Serfaty (Project: Development of a modeling technique for turbulent combustion based on an Eulerian/Lagrangian approach – Phase II, Contract No.: 0050.0080122.12.9). During this work Luís Fernando Figueira da Silva was on leave from the Institut Pprime (CNRS - Centre National de la Recherche Scientifique, France).

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