#### 6 Results and Discussion

In this chapter are presented and discussed the results obtained in the simulations of pairwise mixing stirred reactors (PMSR) using detailed reaction mechanisms and *in situ* adaptive tabulation to solve the balance equations. All the simulations reported in this chapter were performed using double precision, in a workstation with an Intel Xeon processor with 8 cores of 2.53 GHz clock rate, 6 GB of RAM and 8 MB of cache, running Linux 2.6.32 operating system.

#### 6.1 Code Verification

# The PMSR model, the ISAT algorithm and the numerical procedures were implemented in an *in house* code written in ANSI C and Fortran 77 languages. This code uses the thermochemistry routines of Chemkin-II package by Kee et al. (1989) [37], the ODE integration routines of CVODE solver by Hindmarsh & Serban (2006) [29], the numerical linear algebra routines of the GSL package by Galassi et al. (2008) [20] and the random number generation algorithm by L'Ecuyer (1996) [47]. In order to ensure the reliability of the developed code, this section presents verification tests that were conducted.

All verification tests reported in this section use time step of  $\Delta t = 0.1$  ms; solver relative tolerance of  $\varepsilon_{rel} = 10^{-6}$ ; and solver absolute tolerance of  $\varepsilon_{abs} = 10^{-9}$ . Also, these tests are run for K = 500 time steps.

#### 6.1.1

#### **Numerical Integration Verification Test**

The first verification test aims to evaluate the correct implementation of the numerical integration routines. For this purpose, the results of the developed code are compared with those obtained with the CONP code by Kee et al. (1989) [37] in the simulation of an adiabatic constant pressure system.

In this test the reaction of a stoichiometric ( $\Phi = 1$ ) mixture of  $CH_4/Air$ at  $T_0 = 1200$  K and  $p_0 = 1$  atm is considered. The skeletal reaction mechanism shown in Table 6.1, (Yang & Pope, 1998a) [97], with 16 species and 40 reactions, is used to describe the  $CH_4$  combustion with air chemical kinetics. This is the same reaction mechanism used by Pope (1997) [70].

|     | Reaction       |   |                 | $A_i$                  | $\beta_i$ | $E_i$     |
|-----|----------------|---|-----------------|------------------------|-----------|-----------|
|     |                |   |                 | (cm, mol, s)           |           | (cal/mol) |
| 1:  | $H + O_2$      | $\rightleftharpoons$                          | OH + O          | $1.59\times 10^{17}$   | -0.927    | 16874.0   |
| 2:  | $O + H_2$      | $\rightleftharpoons$                          | OH + H          | $3.87 \times 10^4$     | 2.700     | 6262.0    |
| 3:  | $OH + H_2$     | $\rightleftharpoons$                          | $H_2O + H$      | $2.16 \times 10^8$     | 1.510     | 3430.0    |
| 4:  | OH + OH        | $\rightleftharpoons$                          | $O + H_2 O$     | $2.10 \times 10^8$     | 1.400     | -397.0    |
| 5:  | H + H + M      | $\rightleftharpoons$                          | $H_2 + M$       | $6.40 \times 10^{17}$  | -1.000    | 0.0       |
| 6:  | H + OH + M     | $\rightleftharpoons$                          | $H_2O + M$      | $8.40\times10^{21}$    | -2.000    | 0.0       |
| 7:  | $H + O_2 + M$  | $\rightleftharpoons$                          | $HO_2 + M$      | $7.00 \times 10^{17}$  | -0.800    | 0.0       |
| 8:  | $HO_2 + H$     | $\rightleftharpoons$                          | OH + OH         | $1.50 \times 10^{14}$  | 0.000     | 1004.0    |
| 9:  | $HO_2 + H$     | $\rightleftharpoons$                          | $H_2 + O_2$     | $2.50 \times 10^{13}$  | 0.000     | 693.0     |
| 10: | $HO_2 + O$     | $\rightleftharpoons$                          | $O_2 + OH$      | $2.00 \times 10^{13}$  | 0.000     | 0.0       |
| 11: | $HO_2 + OH$    | $\rightleftharpoons$                          | $H_2O + O_2$    | $6.02 \times 10^{13}$  | 0.000     | 0.0       |
| 12: | $H_2O_2 + M$   | $\rightleftharpoons$                          | OH + OH + M     | $1.00 \times 10^{17}$  | 0.000     | 45411.0   |
| 13: | CO + OH        | $\rightleftharpoons$                          | $CO_2 + H$      | $1.51 \times 10^{7}$   | 1.300     | -758.0    |
| 14: | CO + O + M     | $\rightleftharpoons$                          | $CO_2 + M$      | $3.01 \times 10^{14}$  | 0.000     | 3011.0    |
| 15: | HCO + H        | $\rightleftharpoons$                          | $H_2 + CO$      | $7.23 \times 10^{13}$  | 0.000     | 0.0       |
| 16: | HCO + O        | $\rightleftharpoons$                          | OH + CO         | $3.00 \times 10^{13}$  | 0.000     | 0.0       |
| 17: | HCO + OH       | $\rightleftharpoons$                          | $H_2O + CO$     | $1.00 \times 10^{14}$  | 0.000     | 0.0       |
| 18: | $HCO + O_2$    | $\rightleftharpoons$                          | $HO_2 + CO$     | $4.20 \times 10^{12}$  | 0.000     | 0.0       |
| 19: | HCO + M        | $\rightleftharpoons$                          | H + CO + M      | $1.86 \times 10^{17}$  | -1.000    | 16993.0   |
| 20: | $CH_2O + H$    | $\rightleftharpoons$                          | $HCO + H_2$     | $1.26 \times 10^{8}$   | 1.620     | 2175.0    |
| 21: | $CH_2O + O$    | $\rightleftharpoons$                          | HCO + OH        | $3.50 \times 10^{13}$  | 0.000     | 3513.0    |
| 22: | $CH_2O + OH$   | $\rightleftharpoons$                          | $HCO + H_2O$    | $7.23 \times 10^{5}$   | 2.460     | -970.0    |
| 23: | $CH_2O + O_2$  | $\rightleftharpoons$                          | $HCO + HO_2$    | $1.00 \times 10^{14}$  | 0.000     | 39914.0   |
| 24: | $CH_2O + CH_3$ | $\rightleftharpoons$                          | $HCO + CH_4$    | $8.91 \times 10^{-13}$ | 7.400     | -956.0    |
| 25: | $CH_2O + M$    | $\rightleftharpoons$                          | HCO + H + M     | $5.00 \times 10^{16}$  | 0.000     | 76482.0   |
| 26: | $CH_3 + O$     | $\rightleftharpoons$                          | $CH_2O + H$     | $8.43 \times 10^{13}$  | 0.000     | 0.0       |
| 27: | $CH_3 + OH$    | $\rightleftharpoons$                          | $CH_2O + H_2$   | $8.00 \times 10^{12}$  | 0.000     | 0.0       |
| 28: | $CH_3 + O_2$   | $\rightleftharpoons$                          | $CH_3O + O$     | $4.30 \times 10^{13}$  | 0.000     | 30808.0   |
| 29: | $CH_3 + O_2$   | $\rightleftharpoons$                          | $CH_2O + OH$    | $5.20 \times 10^{13}$  | 0.000     | 34895.0   |
| 30: | $CH_3 + HO_2$  | $\rightleftharpoons$                          | $CH_3O + OH$    | $2.28 \times 10^{13}$  | 0.000     | 0.0       |
| 31: | $CH_3 + HCO$   | $\rightleftharpoons$                          | $CH_4 + CO$     | $3.20 \times 10^{11}$  | 0.500     | 0.0       |
| 32: | $CH_4 + H$     | $\rightleftharpoons$                          | $CH_3 + H_2$    | $7.80 \times 10^{6}$   | 2.110     | 7744.0    |
| 33: | $CH_4 + O$     | $\rightleftharpoons$                          | $CH_3 + OH$     | $1.90 \times 10^{9}$   | 1.440     | 8676.0    |
| 34: | $CH_4 + O_2$   | $\rightleftharpoons$                          | $CH_3 + HO_2$   | $5.60 \times 10^{12}$  | 0.000     | 55999.0   |
| 35: | $CH_4 + OH$    | $\rightleftharpoons$                          | $CH_3 + H_2O$   | $1.50 \times 10^{6}$   | 2.130     | 2438.0    |
| 36: | $CH_4 + HO_2$  | $\rightleftharpoons$                          | $CH_3 + H_2O_2$ | $4.60 \times 10^{12}$  | 0.000     | 17997.0   |
| 37: | $CH_3O + H$    | $\rightleftharpoons$                          | $CH_2O + H_2$   | $2.00 \times 10^{13}$  | 0.000     | 0.0       |
| 38: | $CH_3O + OH$   | $\rightleftharpoons$                          | $CH_2O + H_2O$  | $5.00 \times 10^{12}$  | 0.000     | 0.0       |
| 39: | $CH_3O + O_2$  | $\rightleftharpoons$                          | $CH_2O + HO_2$  | $4.28 \times 10^{-13}$ | 7.600     | -3528.0   |
| 40: | $CH_3O + M$    | $\stackrel{\longrightarrow}{\longrightarrow}$ | $CH_2O + H + M$ | $1.00 \times 10^{14}$  | 0.000     | 25096.0   |

Table 6.1: Skeletal reaction mechanism for methane/air combustion.

The evolution of the system temperature/OH mass fraction are shown in Figure 6.1, where it is possible to verify the excellent agreement of the results of the developed code with those obtained with the CONP code by Kee et al. (1989) [37]. These results allow to conclude that the numerical integration routines of the developed code are capable of reproducing the baseline results. The results for the other chemical species, not shown here for the sake of brevity, exhibit a similar agreement.



Figure 6.1: Evolution of T and  $Y_{OH}$  for the first verification test.

#### 6.1.2 Error Control Verification Test

The second verification test evaluates the capacity of the ISAT routines to control the errors. For this purpose, the test analyzes how the error incurred by the ISAT behaves as the value of the ISAT error tolerance is changed.

In this test the PMSR reported in the work of Pope (1997) [70] is considered. This PMSR has its parameters are shown in Table 3.1 and, initially, all of its stochastic particles have their composition set to the adiabatic constant pressure equilibrium of a stoichiometric ( $\Phi = 1$ ) mixture of  $CH_4/Air$  $(T_{eq} = 2376 \text{ K})$  at  $T_0 = 300 \text{ K}$  and  $p_0 = 1 \text{ atm.}$  At every time step, three inflow streams at atmospheric pressure and with mass flow rates in the ratio 0.85 : 0.05 : 0.1 enter the reactor. The first stream is air (79%  $N_2$  and 21%  $O_2$ ) at  $T_{in} = 300 \text{ K}$ , the second one is  $CH_4$  at  $T_{in} = 300 \text{ K}$ , whereas the third stream composition is the same as the particles which initially are within the PMSR. The thermochemistry of these mixtures is also described by the skeletal reaction mechanism of Table 6.2, (Yang & Pope, 1998a) [97].

| number of particles | N       | 100 |
|---------------------|---------|-----|
| residence time (ms) | $	au_r$ | 10  |
| mixing time (ms)    | $	au_m$ | 1   |
| pairwise time (ms)  | $	au_p$ | 1   |

Table 6.2: PMSR parameters used in the code verification tests.

Note that Pope (1997) [70] does not provide details on the actual composition of each particle entering the reactor. Indeed, this three stream problem may be treated in several ways, for instance, each incoming particle may have the same composition, or each incoming particle may be prescribed with the composition of a given stream. Here the first, simpler, possibility is used.

In the simulation of the PMSR described above an ISAT binary search tree with a maximum of 1,000 entries is used as well as an ISAT lower bound of  $\kappa = 1$ .

The error metric used by Pope (1997) [70] to measure the error incurred by ISAT technique is the *global error* over K = 500 time steps, which is defined as

$$\epsilon_G \equiv \frac{1}{KN_p} \sum_{k=1}^K \sum_{j=1}^{N_p} ||\boldsymbol{\phi}^{(j)}(k\Delta t)_{ISAT} - \boldsymbol{\phi}^{(j)}(k\Delta t)_{DI}||_2, \quad (6.1)$$

where the subscripts  $_{DI}$  and  $_{ISAT}$  denote DI and ISAT calculations, respectively. This is the error metric used in this verification test to evaluate the capacity of the ISAT routines control de errors incurred by the algorithm. In order to seek the two time series used to compute  $\epsilon_G$  exhibit a small statistical dispersion, at least in the beginning of the computation, the same seed values are used for the random process describing mixing and outflow.

The behavior of the ISAT global error as function of the error tolerance for the developed code and for the reference PMSR of Pope (1997) [70] (described above) is shown in Figure 6.2. The results show that the linear trend of  $\epsilon_G$  with  $\varepsilon_{tol}$  obtained by Pope (1997) [70] is not recovered, but, instead, a nearly constant value of  $\epsilon_G$ , of the order of  $10^{-1}$ , occurs when  $\varepsilon_{tol}$  is decreased. Such a behavior could be explained by the uncertainty of the particle composition adopted Pope (1997) [70] at the inflow. Another possible explanation for the observed discrepancy is the use of a scaling matrix (Pope, 1997) [70] to construct the ellipsoid of accuracy, Eq.(5.16). This scaling matrix could be responsible for the decrease of the error measure of the enthalpy. As will be show in the next section, the expected error behavior is recovered under more controlled situations. Note also that the monotonically decreasing behavior of  $\epsilon_G$  exhibit by Pope (1997) [70] seems rather surprising for such a small number of stochastic particles, which is expected to lead to large bias errors.



Figure 6.2: Behavior of the ISAT global error as function of the error tolerance for the second verification test.

#### 6.2 Analysis of ISAT Accuracy

In order to assess the accuracy of the ISAT technique implementation, this section defines the error metrics used to estimate the uncertainties in ISAT calculations. Also, this section presents a study which aims to compare the calculation results obtained by the ISAT technique with those issued from the direct integration (DI), which uses CVODE solver to perform the numerical integration of the evolution equation in a PMSR.

#### 6.2.1 Error Metrics

The *absolute global error* of the ISAT calculation over a time interval  $\Delta \tau$  is defined as

$$\varepsilon_g \equiv \frac{1}{\Delta \tau} \int_t^{t+\Delta \tau} || \boldsymbol{B} \left[ \langle \boldsymbol{\phi} \rangle \left( t' \right)_{DI} - \langle \boldsymbol{\phi} \rangle \left( t' \right)_{ISAT} \right] ||_2 dt', \tag{6.2}$$

where  $\boldsymbol{B}$  is a scaling matrix. In this work  $\boldsymbol{B}$  is a identity matrix except by the first entry, which is chosen equal to inverse of the equilibrium enthalpy of the mixture that feeds the reactor. This metric is a global measure of error imposed by the ISAT technique on the solution of the system of ODE's that governs the problem under study.

A metric that represents a local measure of the error incurred by ISAT technique is the *relative local error* of a property  $\psi$ , which is defined as

$$\varepsilon_{r,\psi} \equiv \left| \frac{\psi_{DI}(t) - \psi_{ISAT}(t)}{\psi_{DI}(t)} \right|.$$
(6.3)

Two other metrics, which are used to measure the global error are the mean relative error of  $\psi$  over an interval  $\Delta \tau$ , defined as

$$\langle \varepsilon_{r,\psi} \rangle_M \equiv \frac{1}{\Delta \tau} \int_t^{t+\Delta \tau} \varepsilon_{r,\psi}(t') dt', \qquad (6.4)$$

and the maximum relative error of  $\psi$  over an interval  $\Delta \tau$ , defined as

$$\left\langle \varepsilon_{r,\psi} \right\rangle_{\infty} \equiv \sup_{t' \in [t,t+\Delta\tau]} \{ \varepsilon_{r,\psi}(t') \}.$$
(6.5)

Those metrics were chosen in order to provide measures that are, in a sense, more global than that of Eq.(6.1) and, thus, could be easily applied to more complicated problems, such as those involving transport.

## 6.2.2 PMSR with a $CO/O_2$ Mixture

Consider a PMSR initially filled with a fuel-lean ( $\Phi = 0.7$ ) mixture of  $CO/O_2$ at  $T_0 = 2948.5$  K and  $p_0 = 1$  atm. At every time step, a fuel-lean ( $\Phi = 0.7$ ) mixture of  $CO/O_2$  enters the reactor at  $T_{in} = 300$  K and  $p_{in} = 1$  atm. The constant pressure and enthalpy equilibrium state associated to the inflow mixture is reached at  $T_{eq} = 2948.5$  K. The reaction of CO with  $O_2$ , which chemical kinetics is described by the reaction mechanism given in Table 3.1, involves 4 species and 3 reactions.

#### Influence of the time scale ratio

Two configurations of time scales are studied for this PMSR, which are presented in Table 6.3. For the first configuration of time scales, which defines the first test case,  $\tau_m/\tau_r = 1/2$  and  $\tau_p/\tau_r = 1/2$ , so that the pairwise/mixing time scales are of the same order of magnitude as the residence time, thus allowing to obtain partially stirred reactor (PaSR) conditions. For the second test case, which is defined by the second configuration of time scales presented in the Table 6.3,  $\tau_m/\tau_r = 1/10$  and  $\tau_p/\tau_r = 1/10$ , so that the pairwise/mixing time scales are small when compared with the residence time. Thus, the reactor should behave almost like a perfect stirred reactor (PSR), where the processes of mixing and pairing occur instantaneously. Note that the same seed is used to the pairwise mixing and outflow statistical processes in the DI and ISAT calculations.

|                          |         | Case 1 | Case 2 |
|--------------------------|---------|--------|--------|
| number of particles      | N       | 1024   | 1024   |
| residence time $(\mu s)$ | $	au_r$ | 200    | 1000   |
| mixing time $(\mu s)$    | $	au_m$ | 100    | 100    |
| pairwise time $(\mu s)$  | $	au_p$ | 100    | 100    |

Table 6.3: Parameters used in the simulation of a  $CO/O_2$  mixture in a PMSR.

This study uses a binary search tree with a maximum of 50,000 entries; time step of  $\Delta t = 10 \ \mu s$ ; solver relative tolerance of  $\varepsilon_{rel} = 10^{-6}$ ; solver absolute tolerance of  $\varepsilon_{abs} = 10^{-9}$ ; ISAT error tolerance of  $\varepsilon_{tol} = 10^{-3}$ ; and ISAT lower bound of  $\kappa = 1$ .

Figures 6.3 and 6.4 show the comparison between DI and ISAT computational results for the temporal evolution of the first two statistical moments of the reduced temperature (defined in appendix A) in both cases. The dimensionless time,  $\tau^*$ , shown in these figures is also defined in appendix A.



Figure 6.3: Comparison between DI and ISAT results of ensemble average of reduced temperature for cases 1 and 2.

For case 1 results, which span over a range of 500 residence times, one can observe an excellent qualitative agreement for the ensemble average/variance of the reduced temperature. The ensemble average value rapidly drops from the initial value to reach the statistically steady state regime around  $\langle T \rangle^* = 0.3$ . The ensemble variance rapidly grows, then decreases until it reaches the statistically steady state value around  $\langle T'^2 \rangle^* = 0.13$ . The analysis of the two figures shows that the statistically steady state regime is reached after  $\tau^* = 10$ residence times.



Figure 6.4: Comparison between DI and ISAT results of ensemble variance of reduced temperature for cases 1 and 2.

In case 2, where a range of 250 residence times is computed, one can also observe an excellent qualitative agreement for the ensemble average/variance of reduced temperature. Again, the overall history of the PMSR is the same for DI and ISAT. Similar results, not shown here, were obtained for the other thermochemical properties of the reactors.

Aiming to quantify the discrepancies between the values obtained via DI and ISAT, Figures 6.5 and 6.6 present the evolution of the relative local errors of the statistical moments of  $T^*$  and  $Y_O$ , Eq.(6.3). Concerning the errors associated to the mean physical quantities in case 1, one can observe a large statistical variation due to stochastic nature of the PMSR model, with amplitudes reaching 13%. In case 2, relative errors of the order of 1% can be observed.

|                          | Case 1                                  |   | Case 2                                  |  |
|--------------------------|---|---|---|--|
| $\psi$                   | $\left< \varepsilon_{r,\psi} \right>_M$ | $\langle \varepsilon_{r,\psi} \rangle_\infty$ | $\left< \varepsilon_{r,\psi} \right>_M$ | $\left< \varepsilon_{r,\psi} \right>_\infty$ |
| $\langle T \rangle^*$    | 1.0~%                                   | 13.4~%  | 0.0~%                                   | 0.1~%  |
| $\langle Y_O \rangle$    | 1.2~%                                   | 19.1~%  | 0.1~%                                   | 1.0~%  |
| $\langle T'^2 \rangle^*$ | 1.0~%                                   | 12.2~%  | 0.5~%                                   | 2.0~%  |
| $\langle Y_O'^2 \rangle$ | 0.9~%                                   | 13.0~%  | 0.5~%                                   | 3.2~%  |

Table 6.4: Mean and maximum relative errors for cases 1 and 2, using a binary search tree with 50k entries.

In Table 6.4 are presented error metrics associated to the statistical moments of  $T^*$  and  $Y_O$ . One can observe that the mean error of the average properties is smaller than 1.2% in case 1, and of 0.1% in case 2 only. The mean error of  $T^*$  and  $Y_O$  ensemble variances is rather large in case 1. Concerning the maximum error, the extrema are 19.1% and 3.2% for cases 1 and 2, respectively.

Such high values for the maximum errors could be explained by the existence, in ISAT table, of compositions which are tabulated during the transient regime. An approximation for a reaction mapping, which is in statistically steady state regime, computed around one of these compositions incurs in large errors.



Figure 6.5: Evolution of relative local error for ensemble average of the reduced temperature and of the O mass fraction for cases 1 and 2.

The difference among cases is due to the behavior of each reactor at the statistically steady state regime. Indeed, the behavior of the reactor of case 2 is governed by a competition between the chemical and residence times mostly, therefore the thermodynamical properties steady state probability density function is spread over a smaller range than in case 1, where the mixing and pairing time scales are large. This behavior is illustrated in Figures 6.7 and 6.8, which present the comparison between DI and ISAT computations of the mean histograms, averaged over the last 50 residence times, of the reduced temperature and the O mass fraction for cases 1 and 2. These figures underscore the influence of the controlling parameters of the PMSR, i.e., the time scales ratios, on the thermochemical conditions prevailing within each reactor.



Figure 6.6: Evolution of relative local error for ensemble variance of the reduced temperature and of the O mass fraction for cases 1 and 2.



Figure 6.7: Comparison between DI and ISAT computations of the mean histograms (over the last 50 residence times) of the reduced temperature for cases 1 and 2.

Indeed, the temperature within the reactor of case 2 is such that almost only burned gases are found. On the other hand, case 1 reactor is characterized by a bimodal temperature distribution with a large probability of finding  $T^* = 0.04$  and a broader temperature distribution leaning toward the burned gases. Such a distribution, as it could be expected, is reflected on the  $Y_O$  one, which also exhibits a bimodal distribution.



Figure 6.8: Comparison between DI and ISAT computations of the mean histograms (over the last 50 residence times) of the O mass fraction for cases 1 and 2.



Figure 6.9: Comparison between DI and ISAT results (using different seeds) of reduced temperature ensemble average and the corresponding relative local errors for cases 1 and 2.

#### Influence of the statistical process seed

All the results for cases 1 and 2 shown above use the same seed value for the random number generator in DI and ISAT calculations. However, since the mixing model is statistical in nature, it could be expected that the seed value may influence the ISAT behavior. Therefore, if DI calculation seed is kept fixed and ISAT seed is changed, the results for  $\langle T \rangle^*$  and  $\varepsilon_{r,\langle T \rangle^*}$  are modified. This can be seen in Figure 6.9, where one can observe an increase in the relative local error of  $\langle T \rangle^*$  for both cases.

The analysis of graphs in Figure 6.9 indicates that 1024 particles are not sufficient to guarantee the statistical independence of the results. This hypothesis is also confirmed if one observe the Figure 6.10, where it is possible to see discrepancies in DI and ISAT mean histograms of  $T^*$  for both cases.



Figure 6.10: Comparison between DI and ISAT computations (using different seeds) of the mean histograms (over the last 50 residence times) of the reduced temperature for cases 1 and 2.

On the other hand, these histograms qualitatively are not much different from those shown in Figure 6.7. Thus, one can conclude that although the results have not guaranteed their statistical independence with a sample of 1024 particles, they do not vary much with a sample of this size. Possibly a sample of 4096<sup>1</sup> particles is sufficient to ensure the independence of the results.

#### Influence of the ISAT error tolerance

In the early development of the ISAT technique (Pope, 1997) [70] it was noted that the choice of the tolerance could affect the accuracy of the problem solution. In order to investigate the effect of the tolerance on the present results, Figure 6.11 presents the absolute global error, defined in section 6.2.1,

<sup>&</sup>lt;sup>1</sup>Powers of 4, such as  $1024 = 4^5$  and  $4096 = 4^6$ , are commonly used in statistics since they are always perfect squares, which facilitates the construction of histograms.

as a function of the ISAT error tolerance for cases 1 and 2. When the same statistical seed is used, for both cases,  $\varepsilon_g$  decreases monotonically as  $\varepsilon_{tol}$  is reduced. However, if different statistical seeds are used, one can note a limit where  $\varepsilon_g$  does not decrease if  $\varepsilon_{tol}$  is reduced. This saturation in  $\varepsilon_g$  value indicates that decrease  $\varepsilon_{tol}$  value bellow  $10^{-3}$  is not effective in cases where the statistical seeds are different.



Figure 6.11: Absolute global errors for cases 1 and 2 as function of the error tolerance, using a binary search tree with 50k entries.

From the analysis of the global and local error metrics it is possible to characterize an ISAT table with 50k entries as one with an excellent qualitative reproduction of the results, in which the local errors are less than 20% and the global errors are smaller than 1%.

#### Influence of the ISAT lower bound

Tests were also made to characterize the influence of the ISAT lower bound,  $\kappa$ , on the accuracy of the algorithm. Again equal statistical seed are used for DI and ISAT calculations. Table 6.5 shows the values of absolute global error as function of  $\varepsilon_{tol}$  and  $\kappa$  for a test case similar to case 1, but simulated only for 100 residence times. The analysis of this data reveals that, in general, for a fixed value of  $\kappa$ , the error decreases monotonically as  $\varepsilon_{tol}$  is reduced.

Moreover, one can note that, for a fixed value of  $\varepsilon_{tol}$ , the error remains approximately of the same order of magnitude, except for the pair  $\varepsilon_{tol} = 10^{-6}$ and  $\kappa = 10^9$ . In this case, the lengths of the half-axes of the EOA are limited within a range that varies only two orders of magnitude, Eq.(5.15), which leads to a bad initial estimate for the region of accuracy of the ISAT.

|          |                      |                      | $\varepsilon_{tol}$  |                      |                      |
|----------|----------------------|----------------------|----------------------|----------------------|----------------------|
| $\kappa$ | $10^{-2}$            | $10^{-3}$            | $10^{-4}$            | $10^{-5}$            | $10^{-6}$            |
| $10^{0}$ | $3.3 \times 10^{-3}$ | $2.4 \times 10^{-4}$ | $5.0 \times 10^{-5}$ | $4.1 \times 10^{-6}$ | $3.4 \times 10^{-7}$ |
| $10^{3}$ | $3.3 \times 10^{-3}$ | $2.4 \times 10^{-4}$ | $5.0 	imes 10^{-5}$  | $4.1 \times 10^{-6}$ | $3.4 \times 10^{-7}$ |
| $10^{5}$ | $3.3 \times 10^{-3}$ | $2.4 \times 10^{-4}$ | $5.0 	imes 10^{-5}$  | $4.1 \times 10^{-6}$ | $3.3 	imes 10^{-7}$  |
| $10^{6}$ | $3.3 \times 10^{-3}$ | $2.4 	imes 10^{-4}$  | $5.0 	imes 10^{-5}$  | $4.1 \times 10^{-6}$ | $2.9 	imes 10^{-7}$  |
| $10^{7}$ | $3.3 \times 10^{-3}$ | $2.4 \times 10^{-4}$ | $5.0 \times 10^{-5}$ | $3.5 \times 10^{-6}$ | $4.0 \times 10^{-7}$ |
| $10^{8}$ | $3.3 \times 10^{-3}$ | $2.4 \times 10^{-4}$ | $3.7 \times 10^{-5}$ | $1.2 \times 10^{-6}$ | $5.4 \times 10^{-7}$ |
| $10^{9}$ | $3.3 \times 10^{-3}$ | $2.4 	imes 10^{-4}$  | $3.7 	imes 10^{-5}$  | $3.2 \times 10^{-5}$ | $2.4 	imes 10^{-2}$  |

Table 6.5: Absolute global error as function of  $\varepsilon_{tol}$  and  $\kappa$ .

From these results it may be concluded that the filter of chemical time scales, characterized by  $\kappa$  and originally proposed in this work, does not offer any significative advantage in terms of accuracy of the overall ISAT technique. The effect of this parameter on the side of the binary search tree or the speed-up of the computation are not investigated, although should deserve attention in future works.

# 6.2.3 PMSR with a $CH_4/Air$ Mixture

The third studied case consists of a PMSR initially filled with the combustion products of a stoichiometric ( $\Phi = 1$ ) mixture of  $CH_4/Air$  at  $T_0 = 2100$  K and  $p_0 = 1$  atm. At every time step, a stoichiometric ( $\Phi = 1$ ) mixture of  $CH_4/Air$  enters the reactor at  $T_{in} = 300$  K and  $p_{in} = 1$  atm. The constant pressure and enthalpy equilibrium state associated to this mixture is reached at  $T_{eq} = 2225.5$  K. The reaction of  $CH_4$  with air chemical kinetics is described by GRI mechanism version 3.0 [89], with 53 species and 325 reactions. A discussion of the accuracy of such a mechanism is developed by Orbegoso et al. (2009) [65].

The time scales associated to this PMSR are presented in the Table 6.6. For this choice of time scales, where the ratio between the time of pairwise/mixing and the residence time are the order of one quarter, the reactor is expected to behave like a partially stirred reactor.

This simulation uses a binary search tree with a maximum of 60,000 entries; time step of  $\Delta t = 0.1$  ms; solver relative tolerance of  $\varepsilon_{rel} = 10^{-6}$ ; solver absolute tolerance of  $\varepsilon_{abs} = 10^{-9}$ ; ISAT error tolerance of  $\varepsilon_{tol} = 10^{-3}$ ; and ISAT lower bound of  $\kappa = 1$ . Different seed are used for the DI and ISAT calculations, it can thus be expected that rather large errors result.

Table 6.6: Parameters for a PMSR of  $CH_4/Air$  that behaves like a partially stirred reactor.

| number of particles | N       | 1024 |
|---------------------|---------|------|
| residence time (ms) | $	au_r$ | 4    |
| mixing time (ms)    | $	au_m$ | 1    |
| pairwise time (ms)  | $	au_p$ | 1    |

The comparison between DI and ISAT computational results for the first two statistical moments of the reduced temperature and OH mass fraction for case 3 are presented in Figures 6.12 and 6.13. One can note reasonable and good agreements for reduced temperature and OH mass fraction statistics, respectively. The results of case 3 show large discrepancy for the reduced temperature than that obtained in case 1. The kinetic mechanism of methane is much more complex than the mechanism used to model the carbon monoxide system in case 1, which would in principle lead to a PMSR with methane to assume a wider range of possible thermodynamic states. Thus, it could be expected that the present binary search tree with 60k entries (almost similar to that used in case 1) would yield comparatively lower accuracy.



Figure 6.12: Comparison between DI and ISAT results of the ensemble average of the reduced temperature and OH mass fraction for case 3.

It is noteworthy that a binary search tree with 60k entries uses almost all available memory of the workstation used in this work. Thus, for practical purposes, it is the largest tree that can be used to simulate a PMSR with this methane combustion mechanism and 1024 particles.

In Figure 6.14 one can observe the evolution of the relative local error of the statistical moments of  $T^*$  and  $Y_{OH}$  for case 3. Compared with the results of case 1, the errors of case 3 present more oscillations. The other error metrics for this case are presented in Table 6.7, where it can be noted that the higher



Figure 6.13: Comparison between DI and ISAT results of the ensemble variance of the reduced temperature and OH mass fraction for case 3.

values for average and maximum relative errors in case 3 are 5% and 21%, respectively. Also, the absolute global error for this case is  $2.4 \times 10^{-3}$ , an order of magnitude larger than the values obtained is cases 1 and 2 also using  $\varepsilon_{tol} = 10^{-3}$ .



Figure 6.14: Evolution of relative local error of the first two statistical moments of the reduced temperature and OH mass fraction for case 3.

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Table 6.7: Mean and maximum relative errors for case 3, using a binary search tree with 60k entries.

| $\psi$                              | $\left< \varepsilon_{r,\psi} \right>_M$ | $\left< \varepsilon_{r,\psi} \right>_\infty$ |
|-------------------------------------|---|--|
| $\langle T \rangle^*$               | 3 %                                     | 10 %   |
| $\langle Y_{OH} \rangle$            | 5 %                                     | 16~%   |
| $\langle T'^2 \rangle^*$            | 5 %                                     | 21~%   |
| $\langle Y_{OH}^{\prime 2} \rangle$ | 4 %                                     | 20~%   |

Finally, Figure 6.15 presents the comparison between DI and ISAT computations of the mean histograms, averaged over the last 50 residence times, of the reduced temperature and the HCO mass fraction for case 3.

The temperature PDF presents a bimodal distribution with large probability of finding  $T^* = 1$  and a broader temperature distribution leaning to the fresh gases. On the other hand, the PDF of  $Y_{HCO}$  shows a distribution essentially concentrated in the fresh gases region, and nearly homogeneous elsewhere. This behavior illustrates the fact that HCO, an intermediate species, appears in low concentration at the burned gases.



Figure 6.15: Comparison between DI and ISAT computations of the mean histograms (over the last 50 residence times) of the reduced temperature and HCO mass fraction for case 3.

#### 6.3 Analysis of ISAT Performance

In order to assess the performance of the ISAT technique implementation, this section presents the evolution of the ISAT algorithm outputs (number of additions, growths, retrieves and direct evaluations), the evolution of the height of the ISAT binary search tree and the corresponding rates of change.

#### 6.3.1

#### ISAT Performance for $CO/O_2$ Mixtures

The comparison of evolution of the ISAT algorithm outputs and of the height of the ISAT binary search tree as well as the corresponding rates of change, for cases 1 and 2, which parameters are given in Table 6.3, are presented in Figures 6.16 and 6.17.



Figure 6.16: Evolution of the ISAT algorithm outputs and of the height of ISAT binary search tree for cases 1 and 2.

First one can observe that the number of additions, in both cases, reaches the maximum allowed value in the binary search tree, 50k. Therefore, the additions curve reaches a steady state after  $\tau^* = 5.1$  and  $\tau^* = 1.3$  residence times in cases 1 and 2, respectively. Note that these residence times correspond to 101 and 126 PMSR events (see section 3.5), which indicates that the ISAT table is saturated earlier when the mixing is slow. Figures 6.16 and 6.17 also show the evolution of the height of the binary tree, which reaches steady state after 35 PMSR events ( $\tau^* = 1.8$  residence time) in the first case and 81 PMSR events ( $\tau^* = 0.8$  residence time) in the second case.



Figure 6.17: Evolution of the rates of change of each ISAT algorithm outputs and of the height of the ISAT binary search tree for cases 1 and 2.

It is also noteworthy that in both cases the tree height is one or two orders of magnitude smaller than the total number of entries in the tree ( $\sim$  7k in case 1 and  $\sim$  17k in case 2). This difference between height and total entries in the tree ensures the efficiency of the process of searching for a new query, which may be performed up to seven and three times faster in cases 1 and 2 than a vector search (see section 5.4 for details).

In case 1, Figures 6.16 and 6.17 show that the number of growths presents a sharp rate of change around,  $\tau^* = 2$  residence times, whereas, in case 2, this occurs around  $\tau^* = 6$  times of residence. In both cases, growth steady state occurs after  $\tau^* = 10$  residence times. For case 1, the number of growths is always smaller than the process of additions. This indicates that an increase of the ellipsoids of accuracy, to form a better estimate for the region of accuracy, is not observed. However, this behavior might be circumstantial to the reaction mechanism of the carbon monoxide. This point will not be examined further here.

Figures 6.16 shows that, after tree saturation occurs, the number of retrieves and direct evaluations exceed the number of additions in both cases. In case 1 there is a higher occurrence of the retrieve event, whereas in case 2 direct evaluation prevails. The number of retrieves exhibits a linear limit behavior in both cases. The ISAT behavior for the second case reflects the fact that the binary tree of this case is poor, i.e., contains too few compositions in the region eventually accessed by the calculation. As a consequence, the number of direct evaluations vastly outnumbers the ISAT operations.

As discussed in the appendix B, a necessary condition for a calculation using the ISAT technique to be faster than the same calculation using DI is that the number of retrieves exceed the number of additions by a certain factor, which depends on the specific time of each output. Accordingly the metrics presented in Table B.1, this factor is 9 for  $CO/O_2$  mixtures. From Figure 6.16 it is possible to see that, in case 1, the number of recoveries approximately exceeds the number of additions by a factor of 130, while in case 2 this factor is only 6. Therefore, as case 2 factor is less than 9, ISAT calculations are not expected to be faster than DI procedure.

As can be seen in Table 6.8, where a comparison of computational time is shown, cases 1 and 2 are computed using DI in 4.0 ks and 2.0 ks respectively, whereas with the use of the ISAT, for  $\varepsilon_{tol} = 10^{-3}$ , the same cases spent 2.3 ks and 2.1 ks, respectively. Speed-up factors of 1.7 (case 1) and 1.0 (case 2) are obtained, where the speed-up factor is defined as the ratio between the computational time spent by DI and the computational time spent by ISAT.

Table 6.8 also allows to compare the computational time spent by DI and ISAT for different values of error tolerance. An increase in processing time is obtained as ISAT error tolerance is reduced, which is to be expected, given the fact that lower values of  $\varepsilon_{tol}$  correspond to a smaller region of accuracy. Indeed, as  $\varepsilon_{tol}$  is decreased, it is less likely that ISAT returns a retrieve, which is the ISAT output with lower computational cost. In case 1, for all values of  $\varepsilon_{tol}$ , the ISAT technique offers an advantage in terms of processing time when compared

|                     | Case 1          | -          | Case 2          |            |
|---------------------|-----------------|------------|-----------------|------------|
| $\varepsilon_{tol}$ | time spent (ks) | speed-up   | time spent (ks) | speed-up   |
| DI                  | $\sim 4.0$      |            | $\sim 2.0$      |            |
| $10^{-2}$           | $\sim 1.9$      | $\sim 2.1$ | $\sim 2.1$      | $\sim 1.0$ |
| $10^{-3}$           | $\sim 2.3$      | $\sim 1.7$ | $\sim 2.1$      | $\sim 1.0$ |
| $10^{-4}$           | $\sim 2.4$      | $\sim 1.7$ | $\sim 2.2$      | $\sim 0.9$ |
| $10^{-5}$           | $\sim 2.5$      | $\sim 1.6$ | $\sim 2.2$      | $\sim 0.9$ |
| $10^{-6}$           | $\sim 2.6$      | $\sim 1.5$ | $\sim 2.2$      | $\sim 0.9$ |

Table 6.8: Comparison between the computational time spent by DI and ISAT in cases 1 and 2 and the corresponding speed-up factors.

to the process of direct integration, reducing on average the processing time in 42%. On the other hand, in case 2, no reduction in processing time is seen. As discussed above, this behavior is natural, once the necessary condition for efficiency of the algorithm is not reached.

Aiming to analyze the asymptotic behavior of the ISAT speed-up, case 1 is also simulated for 50,000 time steps. This computation with ISAT spends 204.7 ks, while if DI was used the same calculation would spend  $\sim 1024.0$  ks (speed-up factor of 5.0). Therefore, in this asymptotic case, ISAT spends approximately 80% less time than DI. The pioneer work of Pope (1997) [70] reports an asymptotic speed-up factor of 1000, but this significant factor is not observed in the study developed here.

#### 6.3.2

#### **ISAT** Performance for $CH_4/Air$ Mixtures

The evolution of the ISAT algorithm outputs, height of the ISAT binary search tree and the corresponding rates of change, for case 3, with the parameters shown in Table 6.6, are presented in Figures 6.18 and 6.19. As in cases 1 and 2 the number of additions reaches the maximum allowed value in the binary search tree, 60k for this case. The additions curve reaches a steady state after 160 PMSR events, which corresponds to  $\tau^* = 3.2$  residence times.

The maximum height of the binary search tree for case 3 is  $\sim$  7k as in case 2. Here the steady state of the tree height is observed at  $\tau^* = 1.28$ residence time, or 64 PMSR events, as can be seen in Figures 6.18 and 6.19.

The behavior of the number of growths is quite similar to that of case 1, where the greater rate of change occurs near  $\tau^* = 2$  residence times but, now, the steady state it reached before  $\tau^* = 10$  residence times. For case 3, however, the number of growths is not always smaller than the number of additions.



Figure 6.18: Evolution of the ISAT algorithm outputs and of the height of the ISAT binary search tree for case 3.



Figure 6.19: Evolution of the rates of change of each ISAT algorithm outputs and of the height of the ISAT binary search tree for case 3.

Initially the growths exceed additions by nearly an order of magnitude. After  $\tau^* = 0.2$  residence time the additions exceeded the number of growths, to be overcome again once steady state is reached. This behavior is an indicative that the ellipsoids of accuracy show a considerable period of adaptation, which allows to access with precision a larger portion of the realizable region. This may explain the small discrepancy between the calculations obtained via ISAT and DI presented in section 6.3.1.

As in the previous cases, after the tree saturation, the number of retrieves and direct evaluations exceed the number of additions. The number of direct evaluations overcomes the total number of retrieves in approximately 60%, which is not negligible, but it is far from the large difference that occurs in case 2. This indicates that the binary search tree covers a significant portion of the realizable region in the composition space.

From Figure 6.18 one can estimate as 49 the factor by which the number of additions must exceed at least the number of additions if the ISAT technique is to be more efficient than direct integration.

For case 3, the computational time spent by DI and ISAT is 689.3 ks and 454.5 ks, respectively. Therefore, a speed-up of 1.5 is observed. For this case, other values of the ISAT error tolerance were not tested, since each simulation using the ISAT requires a few days of processing time.

During the simulation of case 3, the evolution of the PMSR was computed during  $\tau^* = 150$  residence times, which corresponds to 7500 PMSR events. Considering that the reactor has 1024 particles, it is possible to note that the system of governing equations defined by Eq.(4.2) is solved 7,680,000 times. In this case ISAT technique allows to save 34% in terms of computational time.

For problems that require solving Eq.(4.2) several times, one should speculate that the ISAT technique would provide an even better performance improvement, since more retrieves are expected and the time per operation of the former is small, when compared to direct integration specific time.

### 6.4

#### Analysis of ISAT Memory Usage

In order to assess the memory usage of the ISAT technique implementation, this section presents an analysis of the memory demanded by the ISAT technique. The amount of memory effectively used in the test cases defined in the section 6.2 is discussed.

## 6.4.1

#### ISAT Memory Complexity

In the simulations that use the ISAT technique, almost all of the memory used is intended for storage of the binary search tree. Therefore, it is desirable to know how to express the memory cost of a binary search tree, such as the one used in ISAT, in terms of the size of the problem under study. In the case of PMSR, the size of the problem is given by  $n_{\phi}$ , which is the dimension of the vector of unknowns.

The operator # (data) receives as input a data type data and returns its memory cost in bytes. The memory cost is generally machine dependent. For instance, in the workstation used in this work, an integer and a double data types respectively have # (integer) = 4 bytes and # (double) = 8 bytes. The standard vector and standard matrix of the ANSI C language have their memory cost given by

$$\#(\texttt{vector}) = n_{\phi} \times \#(\texttt{double}), \qquad (6.6)$$

and

$$\#(\texttt{matrix}) = n_{\phi}^2 \times \#(\texttt{double}), \qquad (6.7)$$

respectively, whereas the GSL package (Galassi et al., 2008) [20] uses its own data structure for vectors and matrices with memory cost given by

$$\# (\texttt{vector}) = 5 \times \# (\texttt{integer}) + n_{\phi} \times \# (\texttt{double}), \quad (6.8)$$

and

$$\#(\texttt{matrix}) = 6 \times \#(\texttt{integer}) + n_{\phi}^2 \times \#(\texttt{double}). \tag{6.9}$$

Although GSL has a high memory cost for basic data structures, such as vectors and matrices, it offers a variety of numerical routines that are robust, stable and well implemented, which justified the choice of this package in the present work.

As seen in section 5.4, each node of the binary search tree stores two elements ( $\boldsymbol{v}$  and  $\boldsymbol{a}$ ) and each leaf stores four elements ( $\boldsymbol{\phi}_0, \boldsymbol{R}(\boldsymbol{\phi}_0, t), \boldsymbol{A}(\boldsymbol{\phi}_0, t)$ ) and  $\boldsymbol{L}$ ).

From the development presented in section 5.2, it is possible to see that matrix  $\boldsymbol{L}$  is lower triangular and requires only  $\frac{n_{\phi}(n_{\phi}+1)}{2}$  floating point positions. But the GSL package does not offer any option of compact matrix storage, which implies that the ISAT implementation presented in this work also uses  $n_{\phi}^2$  floating point positions to store the components of the matrix  $\boldsymbol{L}$ .

It follows that the cost of memory of a **node** and a **leaf** are respectively given by

$$\#(\texttt{node}) = \#(\texttt{vector}) + \#(\texttt{double}), \qquad (6.10)$$

and

$$\#(\texttt{leaf}) = 2 \times \#(\texttt{vector}) + 2 \times \#(\texttt{matrix}). \tag{6.11}$$

Therefore, the memory cost of the ISAT binary search tree (bst) reads

$$\#(\texttt{bst}) = n_L \times \#(\texttt{leaf}) + n_N \times \#(\texttt{node}), \qquad (6.12)$$

where  $n_L$  and  $n_N$  are respectively equal to the number of leaves and nodes in the tree.

#### 6.4.2

#### ISAT Memory Cost for $CO/O_2$ Mixtures

Cases 1 and 2 previously studied are both modeled by a reaction mechanism with 4 species and use a binary search tree with 50,000 entries for ISAT simulations. Hence,  $n_{\phi} = 6$ ,  $n_N = 50,000$  and  $n_L = 50,001$ .

In Table 6.9 is presented a comparison between the memory cost of some of the data types previously presented for cases 1 and 2. The second column presents the amount of memory spent by the ISAT implementation reported in this work (which uses GSL structures) and the third column shows the same information for a hypothetical ISAT implementation (which uses standard ANSI C structures and compact matrix storage strategy). From the data in the table, one can see that for the real implementation  $\#(bst) \cong 40$  Mbytes, whereas for the hypothetical one holds  $\#(bst) \cong 22$  Mbytes. These values lead to the conclusion that the hypothetical implementation would be about 45% more efficient in terms of memory cost than the real approach for cases 1 and 2.

Table 6.9: Comparison between the memory cost of some data types in cases 1 and 2 using two different implementations of the ISAT technique.

|                                | GSL<br>(bytes) | ANSI C<br>(bytes) | difference   |
|--------------------------------|----------------|-------------------|--------------|
| #(vector)                      | 68             | 48                | $\sim 29 \%$ |
| #(matrix)                      | 312            | 288               | $\sim~8~\%$  |
| #(node)                        | 76             | 56                | $\sim 26~\%$ |
| $\#\left(\texttt{leaf}\right)$ | 760            | 405               | $\sim 47~\%$ |

## 6.4.3 ISAT Memory Cost for $CH_4/Air$ Mixtures

Case 3 is modeled by a reaction mechanism with 53 species and uses a binary search tree with 60,000 entries for ISAT simulations. Thus,  $n_{\phi} = 55$ ,  $n_N = 60,000$  and  $n_L = 60,001$ .

The Table 6.10 presents a comparison analogous to that of Table 6.9, but now for case 3. The data of this allows one to see that for the real implementation holds  $\#(\mathtt{bst}) \cong 3.3$  Gbytes, and for the hypothetical implementation  $\#(\mathtt{bst}) \cong 1.8$  Gbytes. The analysis of these values leads one to conclude that, for case 3, the hypothetical implementation would spend about 47% less memory than the real implementation.

|           | GSL (bytes) | ANSI C<br>(bytes) | difference   |
|-----------|-------------|-------------------|--------------|
| #(vector) | 460         | 440               | ~ 4 %        |
| #(matrix) | 24224       | 24200             | $\sim~0~\%$  |
| #(node)   | 468         | 448               | $\sim 4 \%$  |
| #(leaf)   | 49368       | 26620             | $\sim 46~\%$ |

Table 6.10: Comparison between the memory cost of some data types in case 3 using two different implementations of the ISAT technique.

Furthermore, it is noteworthy that the values of memory usage reported in case 3 are not negligible, when compared to the total memory available on the workstation. This underscores what is perhaps the greatest weakness of the ISAT technique, its huge expense of memory.