Study of synthesis gas auto-ignition process by using GQL and QSSA model reduction approaches

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1   Introduction

Mathematical modelling and numerical investigation of auto-ignition processes represent a very complicated branch of combustion theory and its application. The process of ignition is very sensitive to the physical system parameters and to initial and boundary conditions [1]. A very detailed chemical reaction mechanism is typically required to obtain valuable and productive results. This causes two difficulties in the numerical description [1]. One is that typically a large number of elementary reactions between many species appear in the chemical mechanisms, leading to a high dimension of the system of ordinary differential equations (ODEs). The other one concerns the large difference in characteristic chemical time-scales (usually from order of magnitude $O(10^{-10}s)$ to $O(10^{1}s)$) involved due to non-linearity of reaction rates [2]. This increases the stiffness of the mathematical model and requires extreme small time steps during numerical integration. Therefore, both difficulties make computations very demanding in terms of the CPU time and memory storage. Implementing such models for complex flows and geometries, e.g. for 2D or even for 3D reacting flows of engineering / industrial scales remain computationally prohibitive [3]. Thus, the main target of model reduction aims at reducing the dimension and stiffness of the integrated ODE systems.

In this work, two model reduction approaches - the standard Quasi-steady state approximation (QSSA) [4] and the Global Quasi-linearization (GQL) [5] are used to access the dynamics of the synthesis gas combustion system in an auto-ignition problem. The QSSA is based on the assumption that some extremely reactive species stay in a quasi-steady state during the entire combustion process. In contrary the GQL approach [5,6] aims at rigorous definition of combinations of species which as a whole combination can be considered as QSS. Thus, it decomposes the system into fast and slow motions and follows the concept of low-dimensional slow invariant manifolds. Although QSSA has been studied and applied for decades and remains a pivotal tool for model reduction it has several drawbacks [1]. For example, selection of QSS-species relies on the fact that a certain species along is able to represent and to approximate the system slow manifold. The identification of QSS and non-QSS species plays a crucial role for the performance in a wide range of system parameters and conditions [1,7]. Therefore, typically,

this method is assisted with other advanced techniques such as Computational Singular Perturbation (CSP) [8] etc. to verify accuracy and to identify QSS and non-QSS species.

The GQL approach, instead, represents a robust and scaling invariant reduction method, which requires very little *a priori* knowledge about the system behavior and property of species [5]. It allows us automatically identify appropriate combinations of species, which describe reliably relatively fast and slow system dynamics. Therefore, it can be used to study properties of mechanisms of combustion kinetics with subsequent model reduction. The GQL approach has been successfully applied for various mechanisms such as hydrogen, methane, n-heptan and DME combustion systems.

The synthesis gas system, CO-H_2-O_2-N_2 system [9] is considered in this study as an example to illustrate the differences between QSSA and GQL. Although this combustion system is small, it helps us to compare both methods in details. Besides ignition delay times being used to compare and validate the reduced models, also the thermo-chemical state space of the combustion system is investigated and compared. It will be shown that if we obtain GQL and QSSA reduced mechanisms with the same dimension (5 dimension), the GQL reduced chemistry has a much higher accuracy than QSSA for the whole studied range. Furthermore, the 5D GQL reduced chemistry can also predict the state space better than 5D QSSA.

2   Mathematical model

In this study, a pure homogeneous isobaric system of ODEs describing the auto-ignition process is considered. The mathematical model can be expressed in a general vector form as [1, 10]

$$\frac{\mathrm{d}\vec{\psi}}{\mathrm{d}t} = \vec{\mathbf{F}}(\vec{\psi}), \qquad \vec{\psi} \in R^n \tag{1}$$

where $\vec{\psi}$ is the n-dimensional thermos-kinetics state vector as $\vec{\psi} = \left(h, p, \frac{w_1}{M_1}, \cdots, \frac{w_{ns}}{M_{ns}}\right)^{\mathrm{T}}$ and h is the enthalpy, p the pressure and w_i and M_i the mass fractions and molar masses of i-th species. $\vec{\mathbf{F}}(\vec{\psi})$ is the n-dimensional vector of thermo-kinetics source term. Note that although in this work we only consider the isobaric system, the analysis and implementation can also be extended to other systems such as isochoric systems.

3   Suggested framework

In this section, two model reduction techniques are briefly presented and a framework to compare and to investigated the properties of the reduced models is introduced. More information and implementation can be found e.g. in [1,5,6,7].

The QSSA leads to the fact that the rates of consumption of these species are as rapid as they are formed. Therefore, for QSS species ($\vec{\psi}_{QSS}$) remains at quasi-steady state, i.e. their right hand sides of the system of ODEs ($\vec{\mathbf{F}}_{QSS}(\vec{\psi})$) can be approximately set to zero, namely,

$$\frac{\mathrm{d}\vec{\psi}_{QSS}}{\mathrm{d}t} = \vec{\mathbf{F}}_{QSS}(\vec{\psi}) \approx 0, \tag{2}$$

In this way, a low-dimensional manifold of relatively slow motions can be approximated. The GQL approach first explores globally the time-scale hierarchy of the system and decomposes the system into fast and slow subspaces [5]. A global linear transformation matrix $\mathbf{T}_{\mathrm{GQL}}$ is found and used to identify the

fast and slow invariant subspaces. Employing an eigenspace decomposition, one obtains slow ($\tilde{Z}_s$) and fast ($\tilde{Z}_f$) left eigenspaces. Thus similar to the ILDM method [2], the slow manifold can be defined as $\tilde{Z}_f \cdot \frac{d\vec{\psi}}{dt} = \tilde{Z}_f \cdot \vec{\mathbf{F}}(\vec{\psi}) \approx 0$. Then, the following differential algebraic system of equations for the manifold and for the dynamics on the manifold is determined [5,6,7]

$$(Z_s \quad Z_f) \cdot \begin{pmatrix} \tilde{Z}_s \\ 0 \end{pmatrix} \cdot \frac{d\vec{\psi}}{dt} = \vec{\mathbf{F}}(\vec{\psi}). \tag{3}$$

Thus, reduced model for QSSA represents the systems of DAEs as a combination of (1) and (2), while GQL reduced model is represented in form of the system of DAEs (3) [7]. In this manner both reduced models can be investigated and compared. Although both methods focus on identifying the slow and fast variables, QSSA has some drawbacks that GQL easily overcomes:

- The selection of QSS-species is a crucial point for the applications. It is unknown *a priori* if the selection of QSS-species is valid in the application range and hence requires additional efforts to validate the assumption and to check the accuracy of the results. In GQL the slow and fast variables can be identified automatically through the eigenspace decomposition;
- The manifold in the composition system space is not always approximated well by using the QSSA given by (2). The appropriate approximation can be more complicated, e.g. $\tilde{Z}_f \cdot \vec{\mathbf{F}}(\vec{\psi}) = 0$ in GQL approach;
- The validity of QSSA is sensitive to the application range. For example, even for hydrogen oxidation system Williams showed that the QSSA for H is applicable under extremely fuel-lean conditions, while for other conditions it performs poorly. This means one needs different QSSA strategies that can be applied for their corresponding application ranges. The GQL approach, however, is not sensitive to conditions (e.g temperatures, pressures) and system parameters (e.g. mixture compositions), and one GQL reduced chemistry model can be used for a wide application range.

Note that even though several advanced methods such as Computational Singular Perturbation (CSP) have been applied to identify the QSS-species [7, 8] and make more accurate approximations of the slow manifold, in this work, the GQL method is compared to the standard QSSA approach.

4   Results and discussions

In this study, a simple but reliable reaction mechanism [9] for CO-H_2-O_2 combustion system is considered. The Warnatz mechanism of moderate size incorporates 13 species (N_2, CO, H_2, O_2, H_2O, CO_2, OH, H, O, HO_2, H_2O_2, CHO and CH_2O) [9]. Because the system has 4 different elements, namely, N, C, H and O, therefore, the actual reacting space dimension of the ODE system (1) is $13 - 4 = 9$. The detailed chemistry consists of 67 elementary reactions [9]. The application range studied here is $1000 \text{ K} \leq T_0 \leq 2000 \text{ K}$, 1 bar $\leq p_0 \leq 50$ bar and $0.5 \leq \Phi \leq 2.0$. This range covers the range studied in [11] for the ignition delay times of syngas combustion system.

The GQL approach was applied to construct the reduced chemistry. Following the procedures in [7] a 5-dimensional (5D) GQL reduced chemistry model in form (3) was obtained. This 5D GQL reduced chemistry predicts the ignition delay times for the studied range with relative errors less than 2%. A 4D GQL reduced chemistry can also be deduced, but it performs accurately only for a significantly narrower parameter range.

For the syngas system the QSSA can be applied for HO_2, H_2O_2, HCO and CH_2O, as stated e.g. in [9]. This means a 5-dimensional (5D) QSSA reduced chemistry model is also available. Furthermore, other species as QSS-species have been tested as additional candidates for QSS. It was however found that the 5D QSSA reduced mechanism represents the most optimal QSSA reduced model with respect to the accuracy. Adding an additional QSS-species leads to drastic reduction in the performance of the reduced model.

In Fig. 1, the dependence of the ignition delay time on the initial temperature at $p_0 = 1$ bar and stoichiometric mixture composition is shown. Three cases for QSSA where additionally H (yellow lines), O radical (purple lines) or OH (green lines) are considered as a QSS-species. It can be seen that the ignition delay times based on the 5D GQL reduced chemistry (blue line) agrees very well with those obtained by using the detailed chemistry model (shown by circles). The 5D QSSA predicts the ignition delay times very well at high temperatures but large deviations at low temperatures ($T_0 < 1200$ K). The additional QSS-species (here H radical, O radical or OH radical) yielding 4D QSSA reduced models perform with considerably worse accuracy in predicting ignition delay times. The results shown in Fig. 1 indicate, therefore, that the 5D QSSA with HO_2, H_2O_2, HCO and CH_2O as QSS-species defines the reduced model with smallest dimension having a reliable accuracy.
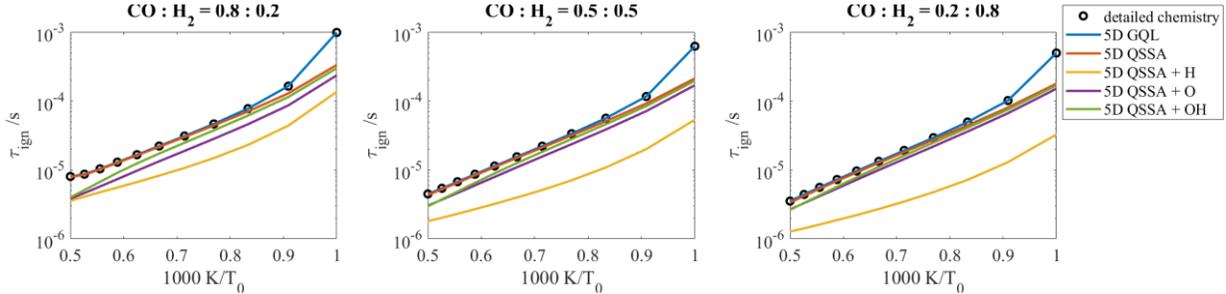
Fig. 1 Dependence of the ignition delay time on initial temperatures for CO/H2=0.8/0.2 (left) , CO/H2=0.5/0.5 (middle) and CO/H2=0.2/0.8 (right) at $p_0 = 1$ bar and stoichiometric mixture composition.

In the following two figures, the ignition delay times for different pressures (Fig. 2) and fuel/air equivalence ratios (Fig. 3) are compared for different CO/H_2 ratios. It shows again that the ignition delay times predicted by 5D GQL agree very well with those by using detailed chemistry. The 5D QSSA predicts good results of ignition delay times at low pressures but large deviations at high pressures. The 5D QSSA predicts the ignition delay times with relative errors from 5% at lean regimes to 12% up stoichiometric equivalence ratios. This confirms additionally that the GQL approach is scaling invariant and therefore is not sensitive to the system parameters and initial conditions.
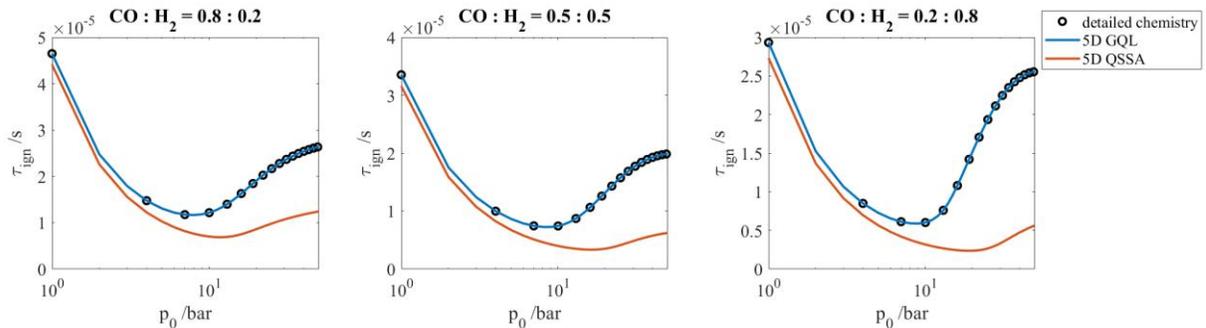
Fig. 2 Dependence of the ignition delay time on initial pressures for CO/H$_2$=0.8/0.2 (left) , CO/H$_2$=0.5/0.5 (middle) and CO/H$_2$=0.2/0.8 (right) at $T_0 = 1300$ K and stoichiometric mixture composition.
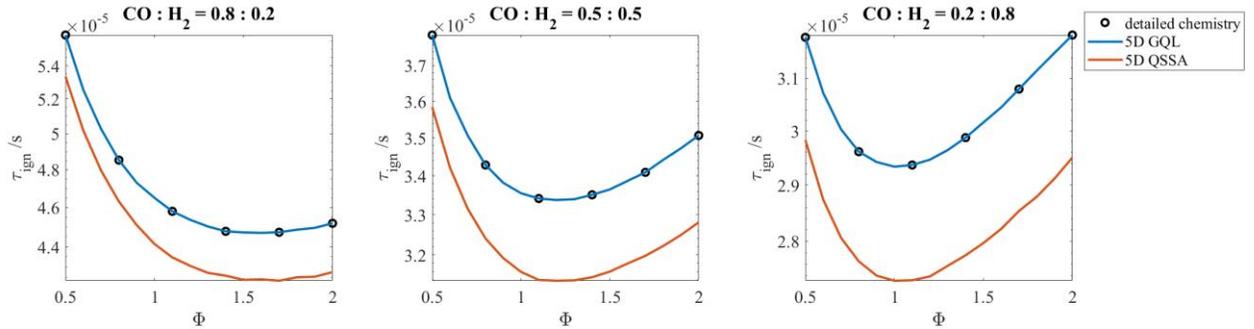
Fig. 3 Dependence of the ignition delay time on fuel/air equivalence ratios for CO/H_2=0.8/0.2 (left) , CO/H_2=0.5/0.5 (middle) and CO/H_2=0.2/0.8 (right) at $T_0 = 1300$ K and $p_0 = 1$ bar.

Although the 5D QSSA has lower accuracy for the prediction of ignition delay times as compared to the 5D GQL, it is still interesting to compare system solutions in the state space. In Fig. 4, the state space of H_2O, OH and CH_2O (QSS-species) is shown versus CO_2. The minimum of CO_2 represents the initial condition and the maximum of CO_2 the equilibrium point. It can be seen for H_2O and OH, there are some deviations between detailed chemistry and 5D QSSA in the initial condition stage, while deviations become smaller for $CO_2 > 3 \cdot 10^{-7}$ mol/kg. This is because the initial state does not belong to the manifold defined by 5D QSSA. Therefore, deviations can be observed near the initial stage of the ignition. For CH_2O, which is a QSS-species, large deviations for $CO_2 < 1 \cdot 10^{-1}$ mol/kg are observed. This means that although CH_2O can be assumed as QSS-species and produces reliable results for ignition delay times, the time histories of CH_2O being constrained to the 5D QSSA are not predicted well enough.

Contrary to the QSSA, the 5D GQL reduced model performs very good in the state space and in time for all stages of the system evolution. It is also interesting to see that the initial stage is also predicted very accurately both for major as well as for minor species. This is because the approximation of the manifold describes initial states of the system extremely well, they belong to or are placed extremely close to the manifold defined by the 5D GQL and the deviations of initial state from the 5D GQL manifold remain negligible [7].

5   Conclusions

In this study, a simple reaction system, namely, the CO-H_2-O_2 system was considered in the auto-ignition problem. In order to study properties of the system dynamics the GQL method was implemented and compared to the standard QSSA. It was shown that a good agreement of ignition delay times between detailed chemistry and reduced chemistry is obtained for a 5 dimensional (5D) GQL or QSSA reduced chemistry model. An additional QSSA for other species such as e.g. H radical, O radical or OH radical leads to loss of accuracy and spoiled performance with respect to the ignition delay times. Similar conclusion can be drawn for 4D GQL, namely, it performs less accurately and can be applied only for a narrower parameter range. Further tests for different pressures and fuel/air equivalence ratios has been performed based on 5D GQL and 5D QSSA showing again that 5D GQL can predict the ignition delay times with higher accuracy having relative errors less than 2% while 5D QSSA has worse performances.

The comparison of the state space evolution shows that the 5D GQL gives a very good agreement with detailed chemistry, while 5D QSSA is only good for certain species such as stable species and non-QSS species. For QSS species, the 5D QSSA performs accurately enough near the equilibrium only. There

were large deviations observed at the initial stage of the ignition processes, while the 5D GQL reduced model performs very accurately in all stages of the detailed system evolution.
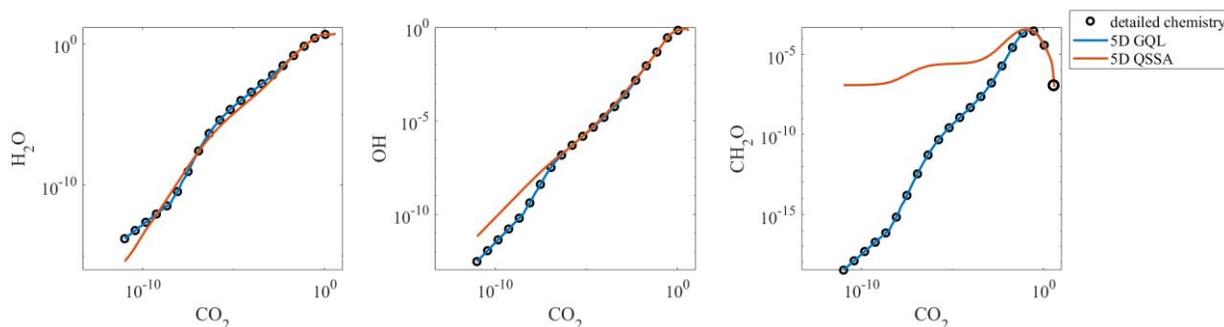
Fig. 4 Projection of the state space onto H_2O-CO_2 (left), OH-CO_2 (middle) and CH_2O-CO_2 (right) for CO:H_2=0.5:0.5 at $T_0 = 1300$ K, $p_0 = 10$ bar and stoichiometric mixture composition.

Acknowledgements

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