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# COMBUSTION SIMULATION AND KINETIC MODELING USING HYBRID REDUCTION SCHEME

By

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A thesis submitted to the

Graduate School-New Brunswick

Rutgers, The State University of New Jersey

In partial fulfillment of the requirements

For the degree of

Master of Science

Graduate Program in Chemical and Biochemical Engineering

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New Brunswick, New Jersey

October, 2015

ABSTRACT OF THE THESIS

Combustion simulation and kinetic modeling using hybrid reduction scheme

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Combustion simulation is a promising tool for multi-disciplines such as fuel development, engine design and emission control. Two biggest challenges confronting us include developing a sufficiently detailed kinetic mechanisms of combustion and formulating numerically implementing models that are capable to capture the essentials but computationally affordable. However, combustion simulations using detailed kinetic mechanisms are often prohibitive in computational fluid dynamics (CFD) due to unaffordable computational cost. Thus, the objective of the research is to reduce the computational intensity of detailed kinetic calculations by an on-the-fly/QSSA hybrid mechanism reduction scheme.

The work consists of two parts: (i) integrating the hybrid reduction scheme in CRUNCH CFD® to enable detailed kinetic calculations; and (ii) applying the hybrid reduction scheme to larger kinetic mechanisms like n-pentane and biodiesel surrogate

methyl butanoate (MB). The models include plug flow reactor (PFR), multi-dimensional engine CFD in KIVA-3V and a supersonic nozzle combustion in CRUNCH CFD®. A fast flux-based QSS species selection method is also employed to quickly select QSS species for various situations. The efficiency and accuracy of the hybrid reduction have been successfully demonstrated according to our results. Aided by fast QSS species selection, the hybrid reduction scheme is efficient to perform complex combustion simulations accurately using large detailed mechanisms.

**ACKNOWLEDGEMENTS**

First of all, I would like to express my deepest gratitude to my advisors, Prof. Marianthi G. Ierapetritou and Prof. Ioannis P. Androulakis, whose encouragement, insightful guidance and great support during my M.S. study helped me to complete my research project. I feel lucky and honored to study combustion simulation, modeling and optimization in their group. I believe that everything that I have learned here today will benefit my life in the future.

I am also heartily thankful to Dr. Shuliang Zhang and Dr. Andrea Zambon. They guided me and gave insightful suggestions about coding, algorithm and technical details for the simulation. This research would not have been possible without their invaluable advice, support and their enormous patience throughout my time at Rutgers University.

Furthermore, I would like to thank Prof. Fuat E. Celik for being my committee member and providing invaluable advice on my work.

Finally, I take this opportunity to convey my sincere thanks to my dear lab mates, my fiancée Runfang, our loving parents, and all of my friends who supported me in any respect during my M.S study.

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# Chapter 1

# Introduction

Reactive flows encompass a wide range of transport phenomena and interact over various scales of time and space, such as combustion, chemical vapor deposition, atmospheric chemistry and chemical processes in flow reactors. Those physical-chemical processes are difficult to solve mathematically due to complex interactions between transport and chemical kinetics. With increasing computational power in recent decades, reactive flow simulations have been widely employed to investigate the details and fundamentals of those complex reactive flows. Among them, combustion simulation is particularly important due to its predictive capability for combustion processes associated with engine, fuel performance, emission, and other environmental concerns. The combustion simulation requires an accurate modeling of chemical kinetics, multiphase flows, turbulence mixing, heat and mass transfer. Two biggest challenges confronting us include developing a sufficiently detailed kinetic mechanisms of combustion and formulating an numerically implementing models that are capable to capture the essentials but computationally affordable.

## 1.1 Combustion kinetic mechanism development

Combustion kinetics is a highly complicated web of species and reactions. Reliable

combustion simulation requires detailed reaction mechanisms to obtain quantitative and sufficiently accurate information about the underlying physical and chemical phenomena. Therefore, much efforts have been put into the development of detailed reaction mechanisms for practical fuels in the past few years (Pitz & Mueller, 2011).

For most hydrocarbon fuels, detailed reaction mechanisms have been already proposed and validated against experimental data. The simplest one is hydrogen mechanism consisting of 3 elements, 9 species and 20 reactions (Petersen & Hanson, 1999). For methane, two widely used mechanisms are GRI-Mech 3.0 (Smith et al.) and Leeds Methane Mechanism (Hughes, Turanyi, Clague, & Pilling, 2001), having over 50 chemical species and 300 reactions. For hydrocarbons with higher carbon numbers, important combustion mechanisms include: C1-C4 alkanes (Marinov et al., 1998), n-pentane and n-heptane (Curran, Gaffuri, Pitz, & Westbrook, 1998), iso-octane (Curran, Gaffuri, Pitz, & Westbrook, 2002) , C8-C16 n-alkanes (Westbrook, Pitz, Herbinet, Curran, & Silke, 2009), and primary reference fuels (PRF) (Curran et al., 2002). Those mechanisms have been widely employed as surrogate mechanisms for practical fuels such as gasoline and diesel fuels in combustion and engine simulations.

In modern engine design and fuel performance testing, two important subjects are predicting ignition delay times and pollutant formation. The above mechanisms mostly estimate ignition delay time and laminar flame speed well over a wide range of reaction conditions, but lack details for pollutant formation. Therefore, many sub-mechanisms have been developed for pollutant formation, such as PAH

(Slavinskaya, Riedel, Dworkin, & Thomson, 2012), GRI $NO_x$ (Smith et al.) and soot formation (Appel, Bockhorn, & Frenklach, 2000; Frenklach, 2002). They are often combined with the above fuel surrogate mechanisms to enable the prediction of pollutants.

Meanwhile, detailed combustion mechanisms are also essential for future energy and power. Recently, increasing attention has been paid to the combustion kinetics of biodiesel and alcohol, since they are clean and renewable biofuels that can relieve the energy crisis and air pollution (Singh, Guldhe, Rawat, & Bux, 2014). Biofuels are complex mixtures and usually have different combustion characteristics due to their different chemical structures and physical properties. Biodiesel, for example, contains mainly five kinds of fatty acid methyl esters, which have unique chemical structures of methyl ester groups with long saturated or unsaturated carbon chains (Herbinet, Pitz, & Westbrook, 2008). Compared with traditional practical fuels, it has oxygen content changing the oxidative kinetics and heating values, as well as different viscosity and volatility for fuel spray and transport phenomena (Pitz & Mueller, 2011). The complexity of biofuels requires more combustion studies aided by reaction mechanisms and computational simulations.

For biodiesels, the most detailed mechanism was proposed by Westbrook et al., consisting of nearly 5000 species and 20000 reactions (Westbrook et al., 2011). Regarding with its huge size, more simple mechanisms were also introduced as surrogate mechanisms to facilitate the computation. Those fatty acid methyl esters with shorter chains were chosen as surrogates instead of using the entire mixture of

biodiesels. The well known surrogate mechanisms include: methyl butanoate (MB) (Fisher, Pitz, Curran, & Westbrook, 2000), methyl decanoate (MD), methyl-5-decenoate (MD5D) and methyl-9-decenoate(MD9D) (Herbinet, Pitz, & Westbrook, 2010). To further enhance the performance, researchers also developed hybrid mechanisms combining two or three surrogates, such as MB+n-heptane (Liu et al., 2013), MD+ n-heptane (Herbinet et al., 2008), and n-heptane+MD+MD9D (Luo et al., 2012). The development of detailed biofuel combustion mechanisms have greatly improved our understanding about chemical kinetics and combustion of those complex mixtures.

### 1.2 Mechanism reduction development

Although detailed mechanisms enabled us to characterize combustion processes accurately, their high complexity and large sizes turned out to be a challenge feature. The computational cost becomes unaffordable and prohibits their applications in the reactive flow simulations with complex transport models. For example, the detailed mechanism of primary reference fuels (PRF) consists of over 1000 species and 4000 reactions, and the biodiesel blend (MD+MD9D+n-heptane) consists of 3299 species and 10806 reactions (Herbinet et al., 2010). It takes huge amount of time to solve such large ODE system of chemical kinetics, not even to mention the time for the transportation and loops over numbers of mesh grids or computational cells. In addition, the reaction rates usually range over several orders of magnitude, resulting

in bad scaling and the mathematical stiffness when solved by the numerical methods and computer software. Thus, it is currently infeasible to use detailed mechanisms in computational fluid dynamics (CFD) and many other reactive flow simulations.

Researchers have proposed various kinetic mechanism reduction approaches to tackle the problem. The core issue here is maintaining the accuracy while reducing the number of species and reactions wisely and in turn the number of ODEs to be solved. Generally, the kinetic mechanism reduction methods can be divided into three categories.

The first category is global reduction or skeletal reduction, where the detailed mechanism is reduced to a skeletal mechanism that is used throughout the entire simulation. Some reduction approaches analyze the sensitivity or control the error induced by the reduction, such as sensitivity analysis (Turanyi, 1990) and mathematical programming (Androulakis, 2000; Perini, Brakora, Reitz, & Cantore, 2012). Some use the flux analysis or a certain pointer to indicate the importance of species and reactions, such as time-integrated flux analysis (Androulakis, Grenda, & Bozzelli, 2004), path flux analysis (PFA) (Sun, Chen, Gou, & Ju, 2010) and entropy production analysis (Kooshkbaghi, Frouzakis, Boulouchos, & Karlin, 2014). Also, one important group of methods are based on the directed relation graph (DRG) method (Lu & Law, 2005). DRG generates skeletal mechanisms by analyzing the dependence of production rates on species. Those species with higher influence on other species production rates will be retained. And there are a series of DRG-based approaches that were developed by combining with other methods, including DRG

with error propagation (DRGEP) (Pepiot-Desjardins & Pitsch, 2008), DRG-aided sensitivity analysis (DRGASA) (Zheng, Lu, & Law, 2007), and DRGEP with sensitivity analysis (DRGEPSA) (Niemeyer, Sung, & Raju, 2010). They further extend the scope of the application, and generate skeletal mechanisms with satisfactory performance. Another important group of methods focus on time-scale analysis for species, including quasi-steady state approximation (QSSA) and partial equilibrium approximation (PEA) (Jones & Rigopoulos, 2007; Lu & Law, 2008; Turanyi, Tomlin, & Pilling, 1993). All the skeletal approaches mentioned above, however, usually generate skeletal mechanisms that are only valid within their defined region of reaction conditions. And therefore a pre-study is usually required to determine the most optimal skeletal mechanism case by case, which can be annoying sometimes for non-professional users. For some simulations where reaction conditions vary in a large scale of time or space, one may need more than one skeletal mechanism to switch.

The second category is adaptive approaches, where a library of reduced mechanisms for different ranges of conditions is developed in the prior analysis. During the simulation, an algorithm will be applied at a certain time-point to search and select an appropriate mechanism from the library according to the range of conditions or other criteria. In-situ adaptive tabulations (ISAT) (Pope, 1997), optimization-based adaptive reduction (Banerjee & Ierapetritou, 2006), and flux-graph adaptive reduction (He, Ierapetritou, & Androulakis, 2008) are well-known examples of this category. Those adaptive reduction approaches consider the different conditions but still require

pre-studies to develop the library.

In order to avoid pre-studies or generating mechanisms beforehand, dynamic adaptive chemistry reduction approaches were introduced to automatically derive a reduced mechanism from the detailed mechanism according to instantaneous conditions at each time-step or local zone. The main challenge here is developing an efficient algorithm that is able to detect when a species becomes active or inactive, but without introducing a new time-consuming analysis module. There are a series of dynamic adaptive chemistry (DAC) method using DRG-based criteria (Liang, Stevens, & Farrell, 2009; Tosatto, Bennett, & Smooke, 2011). Recently, strategies have been also developed such as the tabulation of dynamic adaptive chemistry (TDAC) method (Contino, Jeanmart, Lucchini, & D'Errico, 2011), and the error controlled dynamic adaptive chemistry (EC-DAC) method (Gou, Chen, Sun, & Ju, 2013). The on-the-fly reduction scheme based on element flux analysis (Androulakis et al., 2004; He, Androulakis, & Ierapetritou, 2010b; Zhang, Androulakis, & Ierapetritou, 2013) also belongs to this category, and will be further discussed in the next section. The above dynamic adaptive chemistry methods develop locally accurate reduced mechanisms at each time step with no prior information needed, which is more user-friendly and can be integrated into multi-dimensional CFD to lower the computational costs.

The above mechanism reduction approaches enable us to incorporate detailed kinetic models and mechanisms in the reactive flow simulations, maintaining the accuracy while reducing the computational costs.

### 1.3 Motivation and Outline

As mentioned above, the on-the-fly reduction scheme using the element flux analysis has been proposed to achieve a good accuracy and to reduce kinetic mechanism dynamically (He, Androulakis, et al., 2010b). The on-the-fly reduction calculates the instantaneous element flux between species pairs based on local conditions, and then sort them in descending order. Those species pairs with element flux smaller than a user-defined cutoff value are treated inactive and removed from the reduced mechanism at the current time point. The on-the-fly reduction has been successfully implemented in the plug flow reactor (PFR) combustion simulation, multi-dimensional HCCI engine simulation, and biodiesel combustion simulation with high accuracy and efficiency (He, Androulakis, & Ierapetritou, 2010a; He, Ierapetritou, & Androulakis, 2010; Zhang, Broadbelt, Androulakis, & Ierapetritou, 2012)

The on-the-fly reduction reduces the calculation of kinetic ODEs significantly, but does not reduce the transport calculation since all the species are still involved in the transport model. Therefore, a hybrid reduction scheme has been proposed based on quasi-steady-state approximation (QSSA) and the on-the-fly reduction (Zhang et al., 2013). In QSSA, QSS species' production rates are approximated by zero, so that the ODEs of their production rates become algebraic equations. Their compositions are determined by non-QSS species so that they are not involved in the transport calculation. Meanwhile, those non-QSS species continue being processed by the on-the-fly reduction to reduce the kinetic calculation.

Currently, the hybrid mechanism reduction scheme has been also successfully demonstrated in the PFR and HCCI engine simulations for relatively small mechanisms like methane. It is interesting to extend its applicability and to test the performance for more complex kinetic mechanisms with more species and reactions. In this work, the hybrid reduction scheme will be also implemented in a commercial CFD software, CRUNCH-CFD, to perform simulations using more complex transport models.

The thesis will first include those basic concepts of element flux analysis, on-the-fly reduction and hybrid reduction scheme in Chapter 2. A fast QSS species selection method based on element flux analysis will be also introduced due to its high importance for QSSA and the hybrid reduction. In Chapter 3, the thesis will focus on the implementation of the hybrid mechanism reduction method in CRUNCH-CFD codes. The computational framework will be validated and demonstrated. In Chapter 4, the results will be presented for the extension of our hybrid reduction scheme to more complex reaction kinetics like n-pentane and biodiesel surrogate methyl butanoate (MB). Finally, the major conclusions as well as suggestions will be presented in Chapter 5.

# Chapter 2

# Methodology

Two basic concepts, element flux analysis and quasi-steady state approximation (QSSA), lay the foundation for the hybrid mechanism reduction method presented in the thesis. The above concepts have been already illustrated clearly in our group's previous work (Androulakis et al., 2004; He, Androulakis, et al., 2010b; Zhang et al., 2013). For the completeness of this thesis, some key factors and steps will still be introduced in the following parts.

## 2.1 Transport and kinetics in combustion simulation

The introduction here is aiming to illustrate the equation system in combustion simulation and to know where for us to insert the mechanism reduction scheme to reduce the complexity.

The governing equations for combustion simulations can be presented in different ways, but generally they have two groups of equations. One includes the transport equations for all those continuity, momentum and energy that spatially and temporally solve the thermodynamic state of the mixture. Another group includes the constitutive equations for atomic level processes such as reaction, diffusion and state equations. Detailed discussions can be found in the textbooks, but here we present the a simple summary as follows.

- Momentum

$$\rho\frac{D\mathbf{u}}{Dt}=\rho\frac{\partial\mathbf{u}}{\partial t}+\rho\mathbf{u}\cdot\nabla\mathbf{u}=-\nabla p+\nabla\cdot\tau+\rho\sum_{k=1}^{N}Y_k\mathbf{f}_k \tag{1}$$

- Species continuity

$$\rho\frac{DY_k}{Dt}=\rho\frac{\partial Y_k}{\partial t}+\rho\mathbf{u}\cdot\nabla Y_k=\nabla\cdot(-\rho\mathbf{V}_kY_k)+\omega_k \tag{2}$$

- Energy

$$\rho\frac{De}{Dt}=\rho\frac{\partial e}{\partial t}+\rho\mathbf{u}\cdot\nabla e=-\nabla\cdot\mathbf{q}-p\nabla\cdot\mathbf{u}+\tau:\nabla\mathbf{u}+\rho\sum_{k=1}^{N}Y_k\mathbf{f}_k\cdot\mathbf{V}_k \tag{3}$$

Here, $D$ means the derivative in Eulerian representation; $\rho$ is density; $\mathbf{u}$ is vector of velocity; t is time; $p$ is pressure; $e$ is energy; $\tau$ is viscous stress tensor; $Y_k$ is mass fraction of species k; $\mathbf{f}_k$ is the body force per unit mass; $\mathbf{V}_k$ is the diffusive velocity; and $\omega_k$ is the species production rate.

For the above equations, the mass fractions, velocities and energies have to be considered for all species, which severely increases the feature terms and source terms on the right hand side of equations. In addition, the number of species and reactions is directly related with the number of ODEs for species continuity and kinetic equations.

- One of constitutive equations: the production rate

$$\omega_k=W_k\sum_{r=1}^{R}\left\{\left(v_{k,r}^{''}-v_{k,r}^{'}\right)\left[k_{f,r}\prod_{j=1}^{N}\left(\frac{X_jp}{R_uT}\right)^{v_{k,r}^{'}}-k_{b,r}\prod_{j=1}^{N}\left(\frac{X_jp}{R_uT}\right)^{v_{k,r}^{''}}\right]\right\} \tag{4}$$

where

$$k_{f,r}(T)=A_rT^{\alpha_r}\,exp\left(\frac{-E_{a,r}}{R_uT}\right),\qquad k_{b,r}=\frac{k_{f,r}}{K_{C,r}} \tag{5}$$

Here, $W_k$ is the molecular weight; $X_j$ is mole fraction; $R_u$ is ideal gas constant; $v_{k,r}^{'}$ and $v_{k,r}^{''}$ are reaction stoichiometric coefficients for reactants and products; $k_{f,r}$

and $k_{b,r}$ are rate constants for forward and backward reactions; $K_{C,r}$ is the equilibrium constant; $A_r$ and $a$ are constants in Arrhenius equation.

The kinetic calculation of the production rate requires the detailed reaction mechanisms mentioned in Chapter 1 as well as the mechanism reduction techniques.

## 2.2 Element flux analysis and on-the-fly reduction

In 1994, Revel et al. introduced the element flux analysis (Revel, Boettner, Cathonnet, & Bachman, 1994). It provides a pointer to evaluate and determine the activity of species in a reaction network. Later, the concepts were applied to the mechanism reduction and kinetic analysis (Androulakis et al., 2004), and finally were adopted in the on-the-fly reduction scheme (He, Androulakis, et al., 2010b).

In Equation (6), $\dot{A}_{ijk}$ is defined as the instantaneous element flux of element A from species j (reactants) to species k (products) through reaction i. In Equation (7), $\bar{A}_{jk}$ is the total instantaneous element flux from species j to species k through all reactions.

$$\dot{A}_{ijk}(t) = q_i(t)\frac{n_{A,j}n_{A,k}}{N_{A,i}} \tag{6}$$

$$\bar{A}_{jk}(t) = \sum_{i=1}^{Nr} \dot{A}_{ijk}(t) \tag{7}$$

where $q_i(t)$ is the instantaneous reaction rate of reaction i (mol/s); $n_{A,j}$ and $n_{A,k}$ are the atom number of element A in species j and k; $N_{A,i}$ is the total number of element A in reaction i; and Nr is the number of reactions that involve both species j and k.

For illustration purpose, we take the PFR combustion of methane as an example. Since we are investigating hydrocarbon reactions, carbon flux (C-element flux) is a good target for element flux analysis and sorting. The results of flux analysis and sorting is shown in Table 1.

| Sources | Sinks | Total Instantaneous Carbon flux | Cumulative weight (%) |
|---|---|---|---|
| CH4 | CH3 | 16.8 | 16.8 |
| CO | CO2 | 16.8 | 33.6 |
| HCO | CO | 14.8 | 48.4 |
| CH2O | HCO | 14.2 | 62.6 |
| CH3O | CH2O | 12.2 | 74.8 |
| CH3 | CH3O | 12.1 | 86.9 |
| CH3 | CH2O | 1.9 | 88.8 |
| C2H5 | C2H4 | 1.1 | 90.0 |
| ... | ... | ... | ... |

Table 1 Flux analysis of methane combustion system at a certain time step

If setting a user-selected cut-off value (i.e. 90%), we can identify 8 species pairs as main reactions which are able to describe the main part of the entire chemistry. In brief, a small number of species pairs can capture most of the carbon flux, and only part of the entire reaction network is active.

In the on-the-fly reduction, the total instantaneous flux $\bar{A}_{jk}(t)$ is calculated at each

time point for all possible source-sink species (pairwise species). Those fluxes are sorted in a descending order. Then a user-selected cutoff value is applied to identify those active species and reactions at the current time point. Those species and reactions with larger element flux than the cutoff value will form a reduced mechanism temporally. And then, only those active species and reactions are integrated and solved by the ODE solver, while non-active species are kept at the same concentration for this time point. As the system proceeds to the next time point, the element flux analysis will be repeated again based on the newly solved conditions and then update the set of active species and reactions.

In order to avoid neglecting the active species that in partial equilibrium, He et al. further modified the Equation (7) by Equation (8) for the on-the-fly reduction (He, Androulakis, et al., 2010b).

$$\dot{A}_{ijk}(t) = \left(\left|q_{ifwd}(t)\right| + \left|q_{irev}(t)\right|\right)\frac{n_{A,j}n_{A,k}}{N_{A,i}} \tag{8}$$

In addition, Zhang et al. pointed out that nitrogen element fluxes usually has much smaller values than carbon element fluxes, but they are still essential to capture $NO_x$ emission and cannot be neglected during the on-the-fly (Zhang et al., 2013). Therefore, they calculated and sorted fluxes of different elements separately, and then combined the resulting reduced mechanisms together to form a complete set of reduced mechanism.

The entire on-the-fly reduction does not require any prior study about the reaction mechanism, and the detailed mechanism is used throughout the entire simulation. It is user-friendly and easy to be implemented in CFD codes. One question here is how to

select the cut-off value so that it is able to maintain the accuracy while reduce reaction mechanisms as well as entire computational time to a satisfactory level. The selection is empirical. According to our previous experiences (He, Androulakis, et al., 2010b), a typical value of 99% is suggested for most simulations.

### 2.3 Quasi-steady-state approximation and the hybrid reduction scheme

The practical mechanism like biodiesel surrogates methyl decanoate (MD) have thousands of species and huge numbers of reactions, and CFD simulations still take a long time even though the dynamic reduction approach (on-the-fly) is incorporated (Zhang et al., 2012). There are still too many species involved in transport equations of mass, momentum and energy, though the kinetic calculation time is reduced by the on-the-fly reduction. To further reduce the number of species, Zhang et al. combined a global reduction method, quasi-steady-state approximation (QSSA), with the on-the-fly reduction to form a hybrid mechanism reduction scheme (Zhang et al., 2013).

Turanyi et al. proposed a global reduction method based on the quasi-steady state approximation (QSSA) (Turanyi et al., 1993). According to this method, those quasi-steady state (QSS) species are assumed to reach the dynamic equilibrium quickly where their production rates equal to consumption rates. The net production rates of those QSS species become zero so that their compositions do not change with time. Then, the kinetic ODEs for those QSS species become algebraic equations

because the right-hand side equals to zero, which decreases the calculation complexity. If QSS species are appropriately selected, the solutions obtained from the algebraic equations should be close to original results. More importantly, in QSSA, the concentrations of QSS species are largely determined by the non-QSS species concentrations via algebraic equations, so that QSS species need not to be involved in transport calculations.

In the on-the-fly reduction, those QSS species usually are treated active due to Equation (8) mentioned above. But if we apply QSSA globally, those QSS species are removed ahead of the dynamic reduction, which means that QSSA can further reduce the computation of the on-the-fly reduction as well. In addition, QSSA further reduce the time for the transport part. Thus, we can establish a hybrid computational framework to combine the advantages of global reduction by QSSA and dynamic adaptive reduction by element flux analysis.

During the hybrid reduction, the global QSS species are first identified and selected. In the CFD, only non-QSS species are involved in transport calculations, while QSS species are separated and stored in the computer memory. At each time step, the CFD inputs temperature, pressure and non-QSS species information to the chemistry solver for kinetic calculations. Then, the on-the-fly reduction is applied to those non-QSS species to recognize active non-QSS and active reactions. Since active reactions occur not only between non-QSS species but also include QSS species, the formation of the temporary reduced mechanism and ODEs also need to retrieve QSS species concentrations from the QSS species storage. The chemistry solver will solve those

ODEs to update the temperature and concentrations for active non-QSS species, while the compositions of inactive non-QSS species are kept constant. Then, all non-QSS species concentrations are input to algebraic equations to update the QSS species information. Finally, the updated QSS and non-QSS species are ready for the next iteration. Throughout the entire simulation, only the non-QSS species are considered in the transport calculations, while QSS species are solved internally.

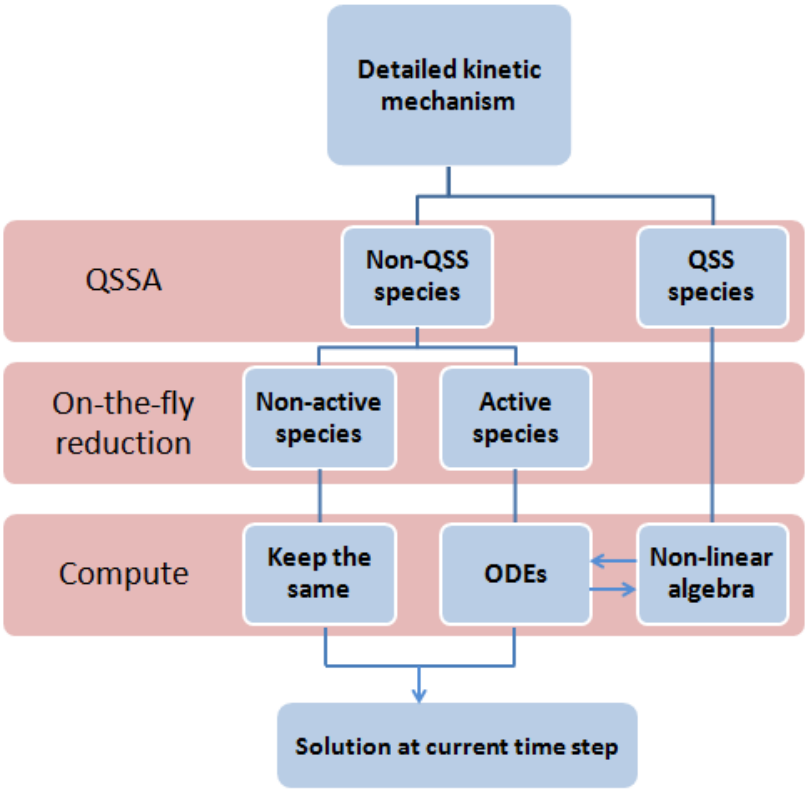



Figure 1 Hybrid reduction scheme

### 2.4 Fast QSS species selection based on element flux analysis

How to select QSS species appropriately is the key question for the hybrid reduction scheme. Currently, there are several well-established methods such as the

computational singular perturbation (CSP) that identify QSS species by the time-scale criteria (Lu & Law, 2008). But they are not easily inserted into our hybrid reduction scheme due to the extra analysis and complex Jacobian matrix operations for their different selection criteria.

In our previous research, a fast flux-based QSS species selection has been proposed, which only takes one-step further based on the total instantaneous flux of species. In QSSA, the global QSS species should have nearly zero net production rate during the whole combustion process. According to Equation (6) and (7), we first analyze the total instantaneous flux $\bar{A}_{jk}(t)$ for all possible species pairs and store the results in an $n \times n$ matrix where n is the number of species. The element flux at $j^{th}$ row and $k^{th}$ column is the flux from species $j$ to $k$, while the flux at $k^{th}$ row and $j^{th}$ column is from species $k$ to $j$. Then the total influx for species j is the summation of $j^{th}$ column, and the outflux is the summation of $j^{th}$ row except for those diagonal entries. As shown in Equation (9) and (10), the influx and outflux of a certain species is defined as follows.

$$\bar{A}_j^{in}(t) = \sum_{k \neq j}^{Nr} \bar{A}_{kj}(t) \tag{9}$$

$$\bar{A}_j^{out}(t) = \sum_{k \neq j}^{Nr} \bar{A}_{jk}(t) \tag{10}$$

The net flux $\bar{A}_j^{net}(t)$ can be calculated by Equation (11), and is always less than or equal to its maximum value during the time of simulation.

$$\bar{A}_j^{net}(t) = abs\left(\left|\bar{A}_j^{in}(t)\right| - \left|\bar{A}_j^{out}(t)\right|\right) \tag{11}$$

$$\bar{A}_j^{net}(t) \leq \max_{0<t<t0} (\bar{A}_j^{net}(t)) \tag{12}$$

The total element flux is a good pointer to represent the species reactivity, and the net flux $\bar{A}_j^{net}(t)$ reflects the production and consumption of a species. If the net flux $\bar{A}_j^{net}(t)$ of a species is always close to zero, the species should have the production and consumption rate in equilibrium, and is potentially a QSS species. Therefore, if the maximum value of the net flux is a very small value close to zero, that species should be a good candidate of global QSS species with nearly zero net production rate during the simulation.

The method has been implemented in PFR combustion model, and is able to select a group of global QSS species by applying an user-defined cutoff value on the maximum net flux. For detailed mechanisms without any references for the QSS species identification, we usually perform the detailed simulation in PFR first, in order to obtain the maximum net flux profile for all species. We select those global QSS species by their maximum net flux profile, then validate those candidates in PFR combustion by checking ignition delay time and composition profiles over a range of conditions. If there is no significant error introduced by those QSS species, they will be used in CFD simulations later.

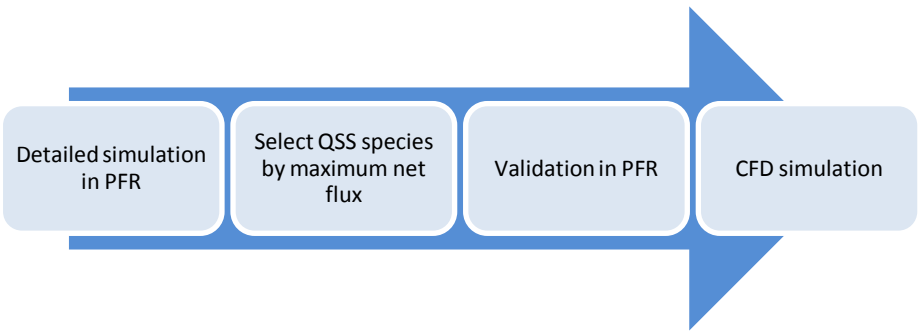



Figure 2 QSS species selection method

This method utilize one property of QSS species that its net production rate is approximately zero, but do not consider its time scale. So it is not strictly based on the mathematical definition of QSSA and can be improved in the future study.

# Chapter 3

# Hybrid Reduction Scheme in CRUNCH CFD®

In this chapter, the hybrid reduction scheme has been implemented in a CFD software CRUNCH CFD® to enable CFD simulations with more complex transport models and high fidelity. CRUNCH CFD® is a multi-physics simulation tool developed by Combustion Research and Flow Technology, Inc. (CRAFT-Tech) for analyzing complex flow problems. It has specialized fluid and thermal solvers and modules including non-ideal equations of state, LES/RANS models and far-field acoustic propagation modules. The computational framework of the new chemistry solver as well as the demonstration by zero-dimensional plug-flow reactor (PFR) and supersonic nozzle flame will be presented in the following sections.

## 3.1 Computational framework

The new chemistry solver with the hybrid reduction mode is now incorporated in the compressible fluid module as the stiff chemistry solver of CRUNCH CFD®. All the CFD/hybrid reduction codes were written in Fortran 77 format. CHEMKIN is used to manage and process reaction mechanism, and DVODE solves the ODEs. The algebraic solver for nonlinear algebraic equations is based on the C05NBF in the Fortran library of Numerical Algorithm Group (NAG). The NAG solver has been regrouped and optimized to meet the technical requirements by CRUNCH CFD®. The

computational framework is summarized in Figure 3.

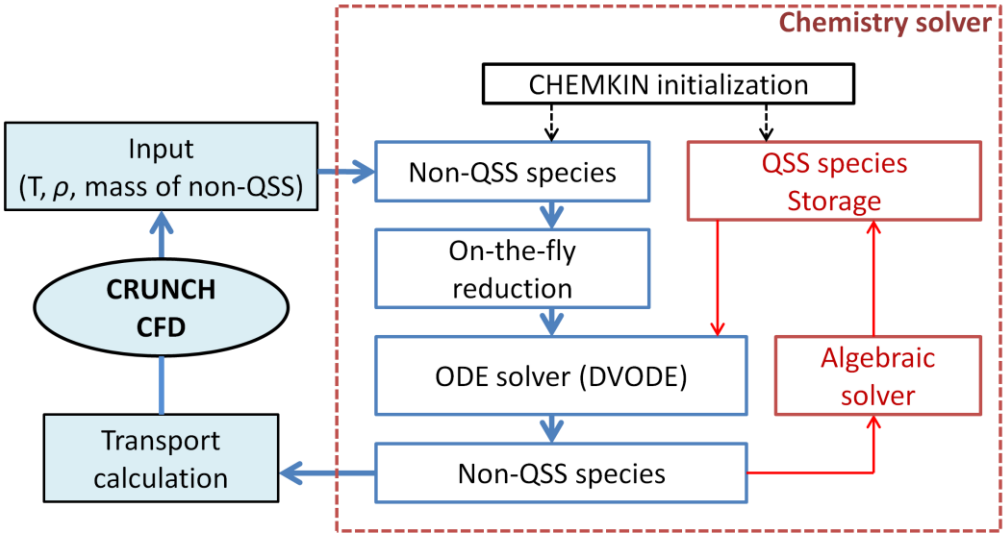



Figure 3 CRUNCH CFD® new hybrid chemistry solver

As mentioned in Chapter 2, only non-QSS species are involved in the transportation between different computational zones and grids. At each computational grid, CRUNCH CFD® executable solves the transport equations and passes variables to the new chemistry solver. The new chemistry solver performs the hybrid reduction and updates the interfacing variables like mass fraction, density, temperature and time. The dual-mechanism implementation proposed by Zhang et al. has been applied in the new chemistry solver (Zhang et al., 2013). In the beginning of the program, CHEMKIN initializes two CHEMKIN-format mechanisms and stores them in common block variables at the same time. One CHEMKIN-format mechanism consisting of only non-QSS species will be used for CFD initialization, transport calculations and also serve as the input for QSS species identification. Another detailed mechanism is the workspace that is used internally in the chemistry solver to

provide information for kinetic equations and elemental analysis.

Currently, there are three modes available: detailed, QSSA-only and hybrid reduction mode. Users can define the cutoff value for on-the-fly reduction, switch mechanisms and test the chemistry solver by a simple PFR combustion case.

### 3.2 Demonstration by hydrogen oxidation simulations

The computational framework was first demonstrated by a hydrogen oxidation mechanism (Petersen & Hanson, 1999) with 9 species and 20 reactions. The aim was to validate the accuracy and to test the new chemistry solver. Two different flow models were used for the demonstration, including a combustion at a single grid and a 2D supersonic nozzle combustion.

The single grid PFR simulation was conducted with the initial temperature 1510K, initial density $0.01921 g/cm^3$. The hydrogen/air mixture was used with $H_2$ 0.0155, $O_2$ 0.123, and $N_2$ 0.8615 in mass fraction.

According to the element flux analysis by the new solver, the maximum net element flux of hydrogen was summarized in Figure 4. It indicated that the net element fluxes and production rates of those intermediate species were relatively large and did not approximate to zero. No QSS species should be selected in this case, otherwise the mixture cannot be ignited properly. Therefore, all 9 species in hydrogen mechanism were maintained throughout the transport and the chemistry calculation. The new chemistry solver was initiated without selecting any QSS species.

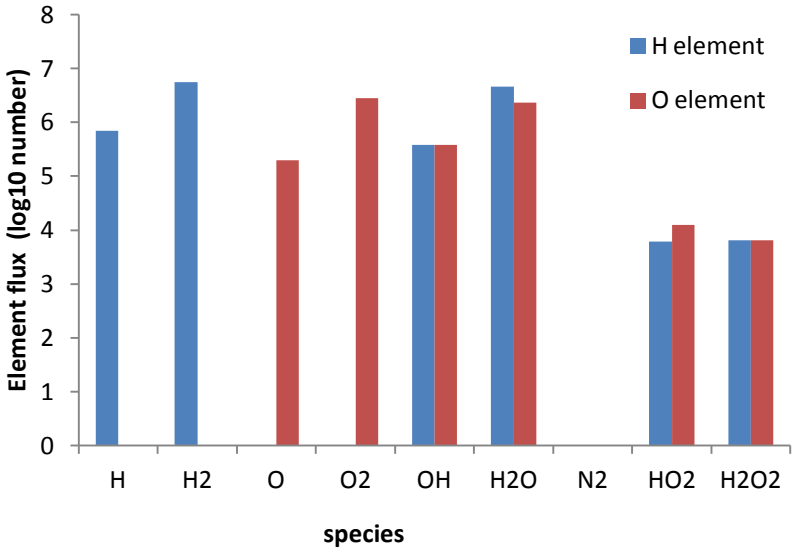
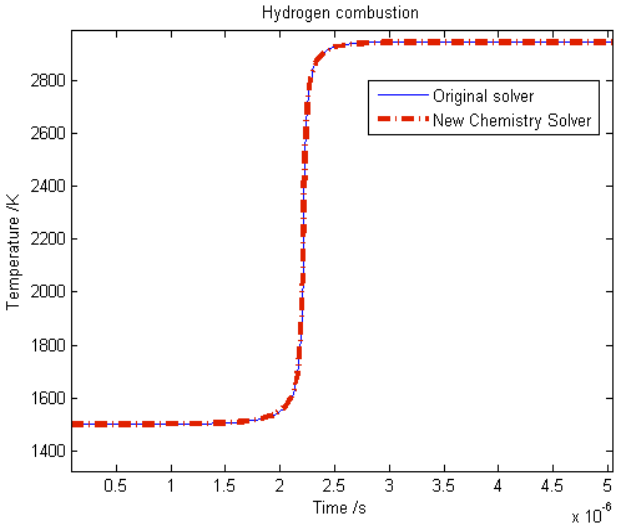



Figure 4 Hydrogen element net flux

Figure 5 shows the temperature and mass fractions of major species ($H_2$, $O_2$, $H_2O$, OH) by the new hybrid reduction solver and the original solver. The results suggest the same accuracy and precision between the original and new chemistry solver. It also confirmed that basic equations, matrices, ODE solver and CHEMKIN were incorporated properly in the new chemistry solver.



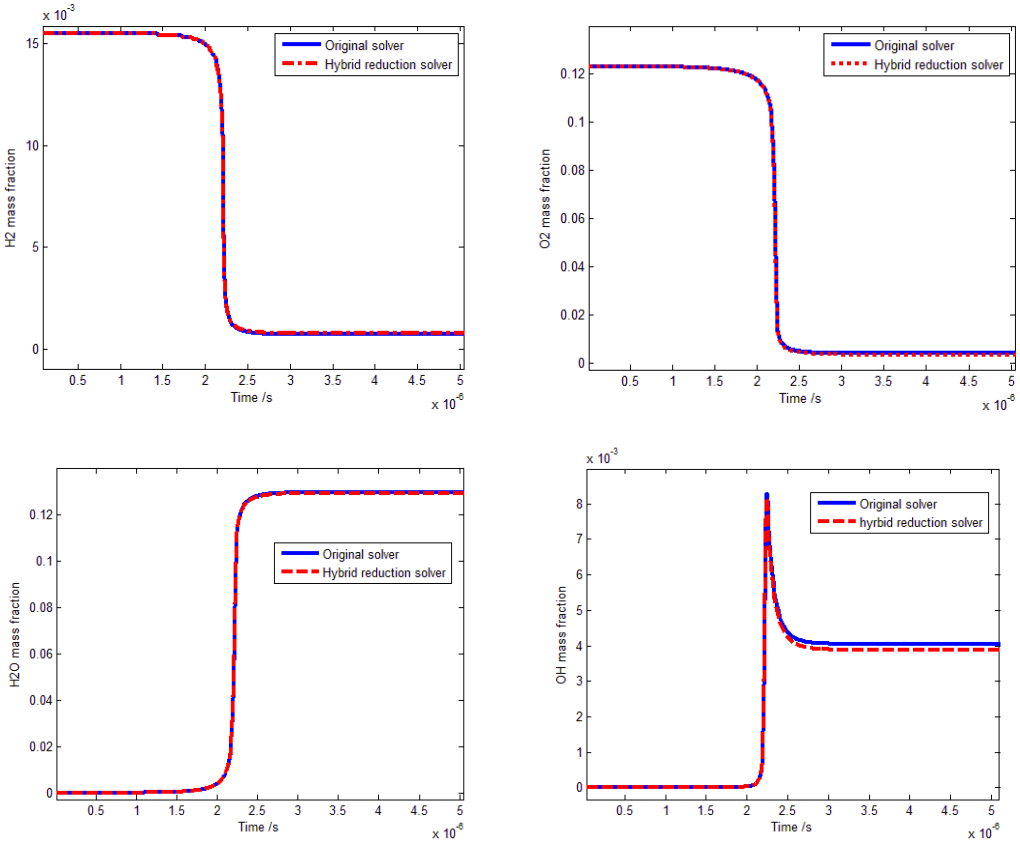



Figure 5 Temperature and major species profile of hydrogen

To further validate the communication of the interfacing variables between the hybrid reduction solver and the CFD code as well as the operational stability, a gas-phase hydrogen/air supersonic nozzle was simulated. Both the original and our newly developed chemistry solver were employed in the CFD code under parallel computation using 8 CPU cores. The case was a supersonic nozzle and $H_2/O_2$ injector model based on a NASA technical paper (Evans, Schexnayder, & Beach, 1978), and was provided by CRAFT Tech.

Figure 6 shows the simulation results of temperature, density and species mass fractions in the upstream part of the injector combustion. The upper figures were from the original solver, and the lower ones were by the new solver. The results by the new

solver agree well with those detailed profiles by original solvers, indicating that the new hybrid reduction solver is ready for combustion simulations in CRUNCH CFD®.

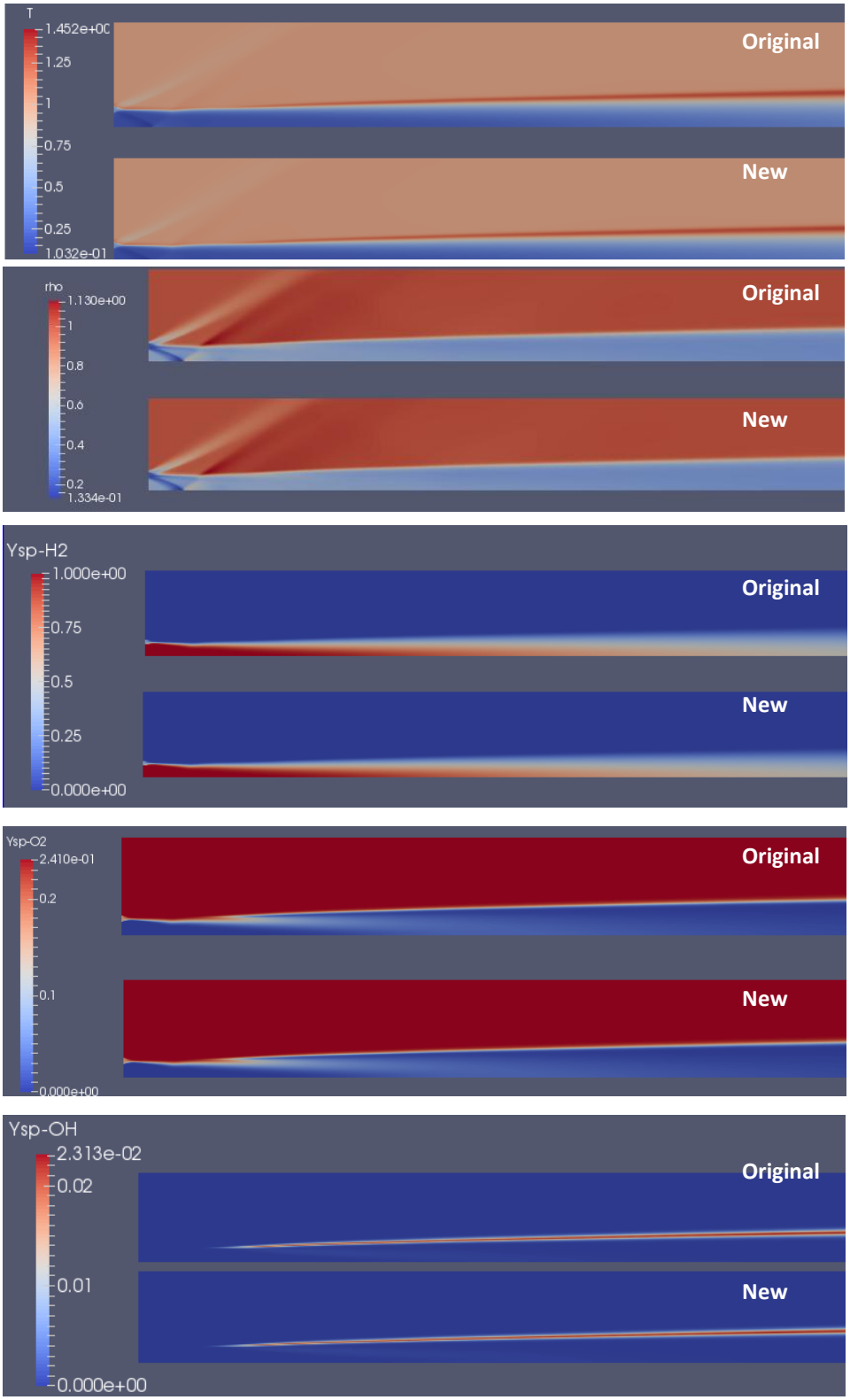



Figure 6 Hydrogen/oxygen supersonic nozzle combustion

### 3.3 Demonstration by methane

The previous simulations used the most simple hydrogen mechanism. All species were involved throughout the simulation and no QSS species were selected for QSSA reduction. Therefore, it was not adequate for demonstrating the performance of the on-the-fly/QSSA hybrid reduction. The next step is to demonstrate the QSSA and reduction of time in transport using a more complex and larger chemical mechanism.

In this work, we choose the methane mechanism GRI-Mech 3.0 with 53 species and 325 reactions. The detailed methane mechanism was prohibitive in CRUNCH CFD® previously due to its large size exceeding the workspace limit of transport calculation. But now, the CFD code with the hybrid reduction enables the incorporation of detailed methane mechanism.

In this demonstration, QSS species selection is conducted using the similar conditions of previous hydrogen case. Then, those selected QSS species are validated in the zero-dimensional PFR combustion using hybrid reduction in CRUNCH CFD®. The two-dimensional $CH_4/O_2$ injector CFD model is still being modified, and will not included in this thesis.

Firstly, the fast flux-based QSS species selection was performed in an PFR with initial temperature 1000K and pressure 57 atm. The detailed simulation using full mechanism GRI-Mech 3.0 was performed. The mass fractions of methane, $O_2$, $N_2$ were in fuel/air equivalence ratio 0.5. The maximum carbon and nitrogen net flux for all species were calculated and summarized in Figure 7.

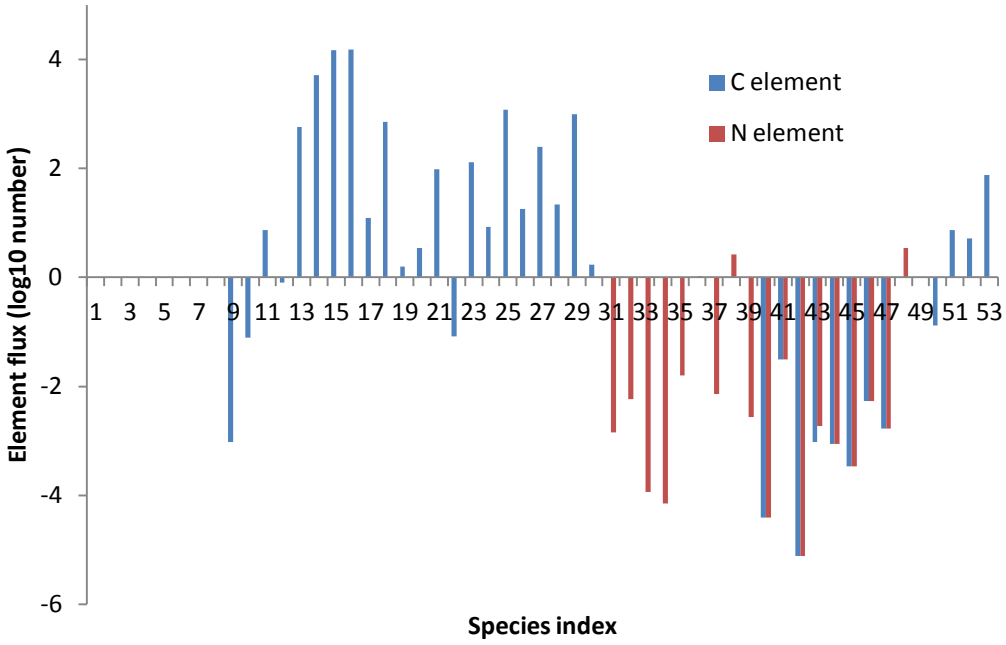



Figure 7 GRI-mech 3.0 element net flux

Four groups of species with small maximum net element flux were selected as QSS species candidates in Table 2. Carbon and nitrogen species were sort in an ascending order by element fluxes of carbon and nitrogen separately, since their flux scale was different.

| **QSS species** | **Carbon species** | **Nitrogen species** |
|---|---|---|
| **2** | C | $H_2CN$ |
| **7** | C, CH, $C_2H$, $C_3H_7$ | $H_2CN$, CN, $NH_3$ |
| **12** | C, CH, $C_2H$, $C_3H_7$, $CH_2(s)$, $CH_2OH$, HCCOH | $H_2CN$, CN, $NH_3$, $NH_2$, HOCN |
| **15** | C, CH, $C_2H$, $C_3H_7$, $CH_2(s)$, $CH_2OH$, | $H_2CN$, CN, $NH_3$, $NH_2$, |

| | |
|---|---|
| HCCOH, $CH_2$, $C_2H_3$ | HOCN, HCNO |

Table 2 GRI-Mech 3.0 QSS species selection

The flux-based QSS selection quickly identified some similar QSS species as those in the literature (Lu & Law, 2008; Montgomery, Yang, Parkinson, & Chen, 2006; Zhang et al., 2013). In addition, more similarity will be obtained if we include more QSS species. For comparison, we also listed QSS species by other methods in Table 3.

| **Selection method** | **QSS Species (only carbon)** |
|---|---|
| **Flux-based** | C, CH, $CH_2$, $CH_2$(s), $CH_2OH$, $C_2H$, $C_2H_3$, HCCOH, $C_3H_7$ |
| **CARM-based** | C, CH, $CH_2$, $CH_2$(s), HCO, $CH_2OH$, $C_2H$, $C_2H_3$, $C_2H_5$, HCCO, HCCOH, $C_3H_7$, $CH_2CHO$, $CH_3CHO$ |
| **CSP-based** | C, CH, $CH_2$, $CH_2$(s), HCO, $CH_2OH$, $CH_3O$, $C_2H_3$, $C_2H_5$, HCCO, $CH_2CHO$ |
| **DRG** | C, $C_2H$, HCCOH, $C_3H_7$, $C_3H_8$, $CH_3CHO$ |

Table 3 QSS species selected by different methods

QSS species are still often selected by various automatic or semi-empirical approaches that are based on different properties of QSS species: (1) low species concentration, (2) short life time and (3) small net production rate. Our method belongs to net production rate methods. For automatic selection using a certain algorithm, however, none of the above is the sufficient condition to identify QSS

species. For time-scale or production rate method, we may mistakenly include species in partial equilibrium reactions, inducing errors in algebraic solver (Lu & Law, 2008; Turanyi et al., 1993). For concentration criterion, not all low concentration species are good QSS species, e.g. $CH_3OH$ and $CH_2CO$ in methane combustion. Including them in QSS species will cause significant errors. Their concentrations are low but not able to reach QSS before the time of ignition. Although our selection roughly identified some QSS species, we further validated them in PFR simulations.

Four sets of QSS selections were then tested in the zero-dimensional PFR combustion in CRUNCH CFD®. The same initial conditions were used in the simulation.

Firstly, the four sets of QSS selections were tested in PFR with only the application of QSSA. From Figure 8 , the temperature profiles shows a good agreement between the QSSA-only simulations and detailed simulation. All four sets of QSS species can be used in the hybrid reduction later.

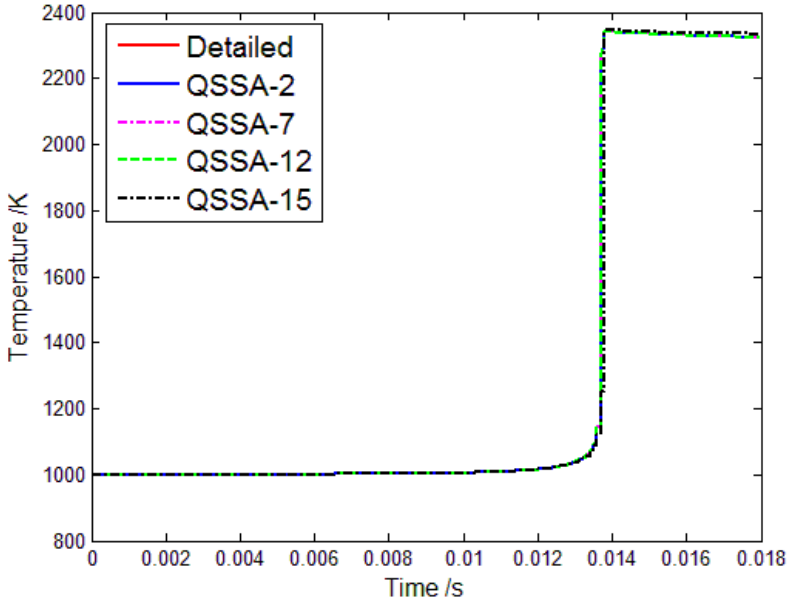



Figure 8 Temperature of QSSA-only mode for methane

Next, the on-the-fly reduction was validated. From Figure 9, the results with only the on-the-fly reduction shows the trend that the accuracy increased with the increasing on-the-fly cut-off value, which is also in accordance with our previous work. In addition, the tiny gap between the results of hybrid and detailed runs (without any reduction) depends largely on the cut-off value of the on-the-fly reduction.

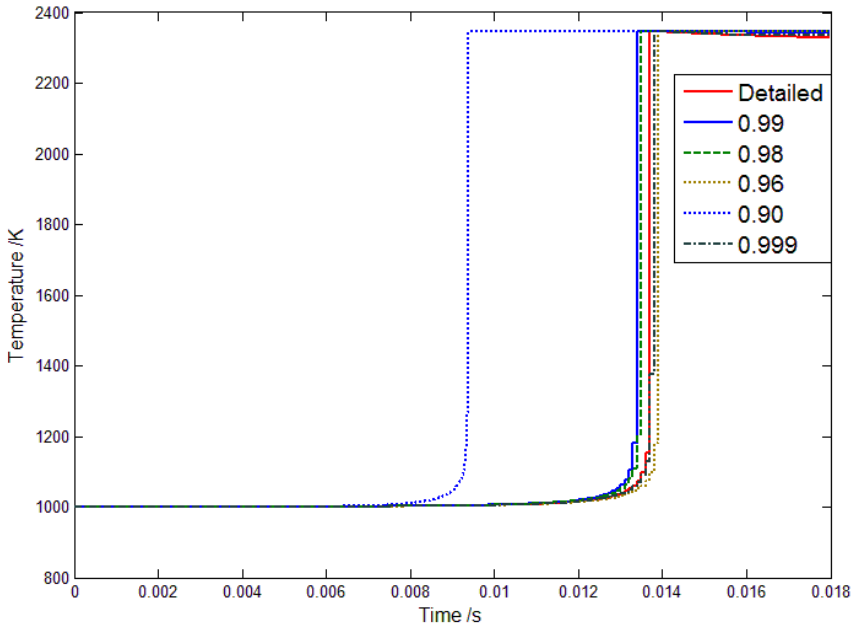



Figure 9 Temperature of on-the-fly mode for methane

Finally, the temperature and species profiles of the on-the-fly/QSSA hybrid reduction were shown in Figure 10. In the hybrid reduction, the temperature of four sets of QSS selections were close to the profiles by the detailed mechanism. For carbon species profiles, there is no significant deviation between results of hybrid reduction and detailed simulation, indicating the correctness of carbon species selected in the QSS species selections. However, for 15 QSS species selection, the mass fraction of NO deviates from other results during the ignition. Compared with the 12 QSS species,

there is a newly selected N-species, HCNO. Therefore, the deviation should be related with the assumption of QSS species, HCNO.

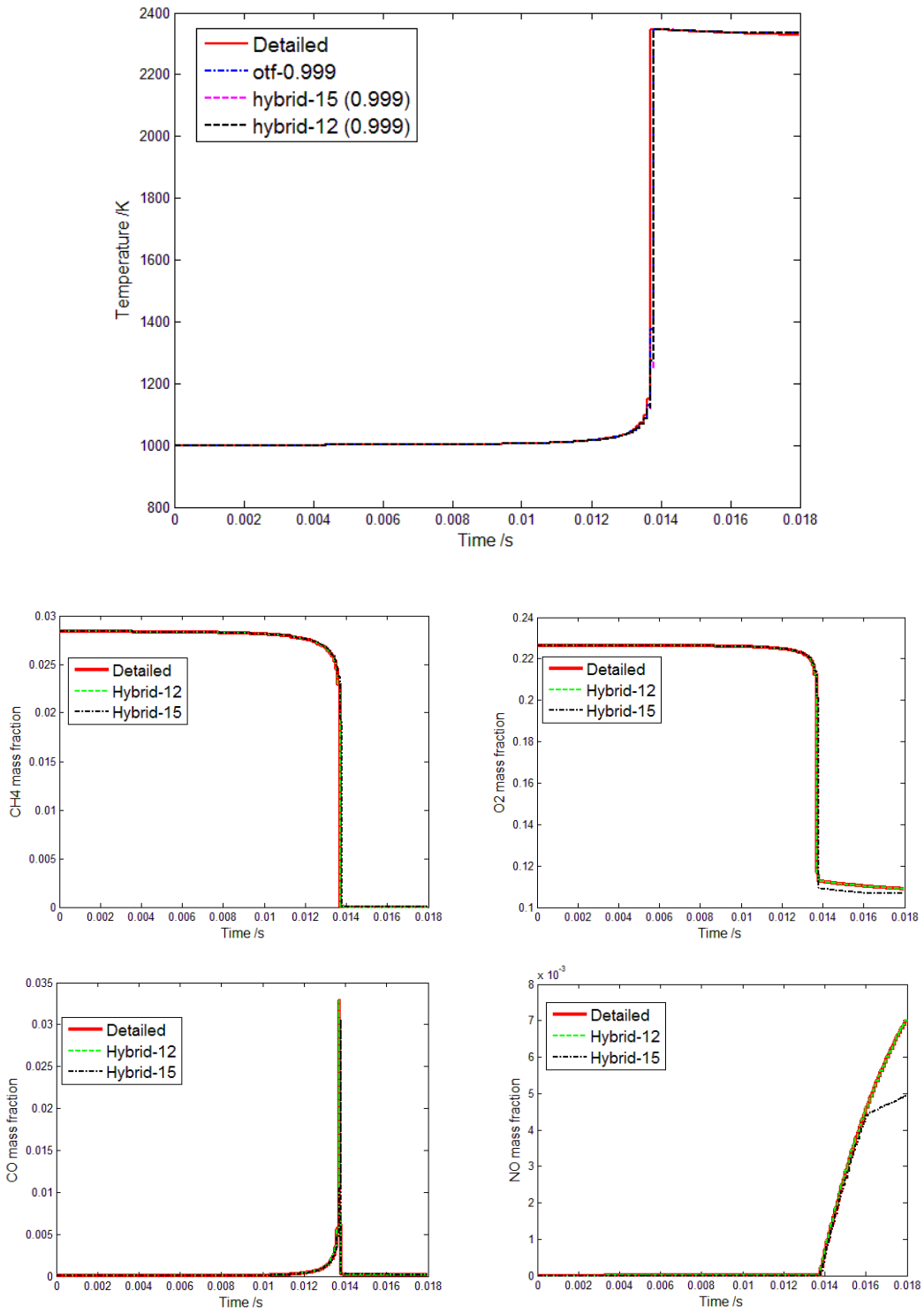



Figure 10 Hybrid reduction for methane

From the CPU-time analysis, the time for solving ODEs decreased significantly after the hybrid reduction applied. The time to solve non-linear algebraic equations increased for those selections with more QSS species, and also caused the total time increased slightly. With more QSS species selected, the extra savings for ODEs were not significant, which probably was due to the stiffness occurred. However, the current PFR model does not consider complex transport calculations, so the final performance in CFD should be optimistic if we consider the time reduced for transport.

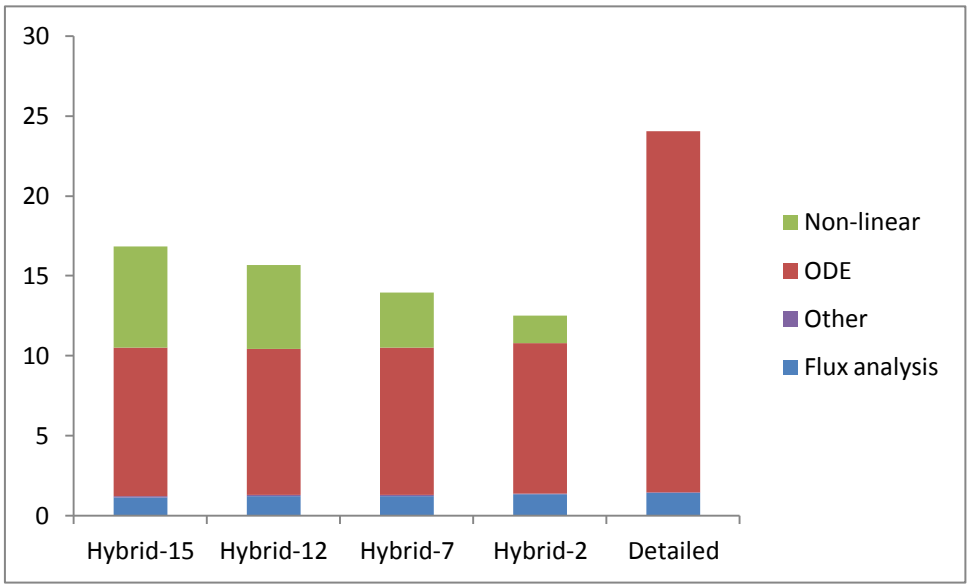



Figure 11 CPU time analysis for new hybrid solver in CRUNCH CFD®

### 3.4 Conclusions

In this chapter, the hybrid reduction framework has been incorporated successfully in CRUNCH CFD® and then demonstrated by both hydrogen and methane oxidation mechanisms. Aided by the flux-based QSS species selection, the new chemistry solver

was able to capture combustion characteristics accurately and to perform detailed simulations at a low computational cost. The zero-dimensional PFR and supersonic injector combustion of hydrogen validated the CFD code with the new chemistry solver. The methane combustion in PFR further verified the correctness of hybrid reduction in CRUNCH CFD® as well as the QSS species selection method. The on-the-fly/QSSA hybrid reduction not only reduce the total number of species for kinetic and transport calculations, but also enable the detailed simulations of larger mechanisms in CRUNCH CFD® that has a limitation on the number of transported species.

The next step is to apply the hybrid reduction in supersonic injector combustion for detailed methane mechanism in CRUNCH CFD®. In the future, more complex transport models will be used with the hybrid reduction in CFD to help us investigate the realistic combustion phenomena.

# Chapter 4

# Hybrid Reduction with Larger Mechanisms

The goal of the research is to extend the applicability of hybrid reduction to more realistic simulations in CFD and larger complex kinetic mechanisms. Despite of the incorporation of the hybrid reduction scheme in CRUNCH CFD®, there was also continuous progress for applying the scheme on larger detailed mechanisms in adiabatic PFR simulations and multi-dimensional engine CFD simulations in KIVA-3V. In this chapter, two larger detailed mechanisms, n-pentane and methyl butanoate (MB), will be used to demonstrate the flux-based QSS species selection and the hybrid reduction scheme in simulations.

## 4.1 Demonstration with n-pentane mechanism

The detailed chemical mechanism n-pentane-nox was developed based on the n-pentane (Curran et al., 1998) and $NO_x$ sub-mechanism in GRI 3.0 (Smith et al.), with 399 species and 1948 reactions in total. The computational frameworks for PFR simulation and KIVA-3V have been adapted accordingly.

### 4.1.1 QSS species selection for n-pentane

In the beginning, the QSS species were chosen according to the maximum net element flux by using the detailed mechanism. The carbon net flux for each species in

n-pentane-nox mechanism was calculated in the PFR simulation. The PFR simulation was carried out with the initial temperature at 950K, pressure 9.6atm and the fuel/air mixture equivalence ratio of 1.0. The maximum carbon net flux of the entire simulation for each species was plotted in Figure 12.

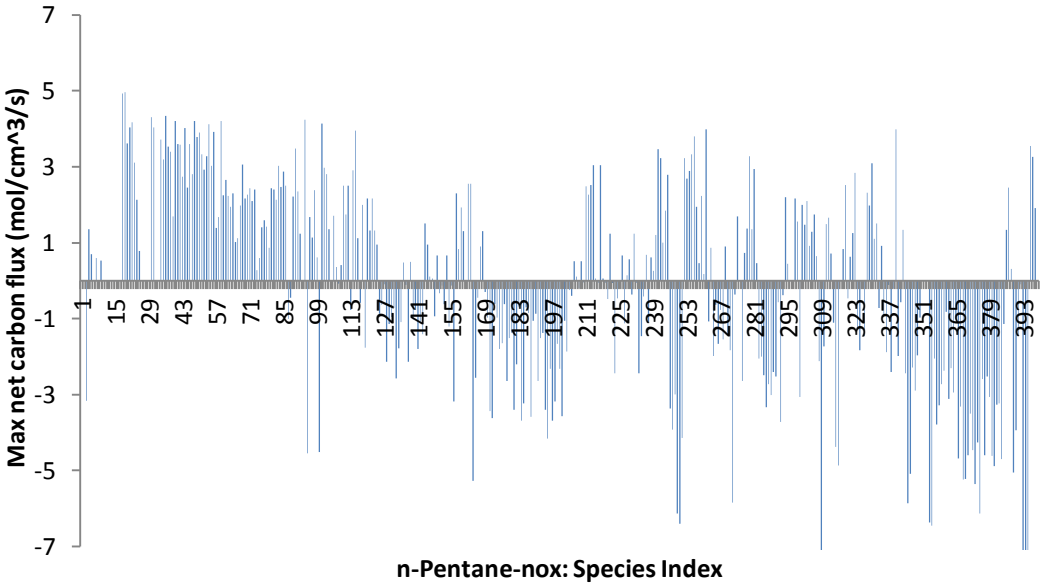


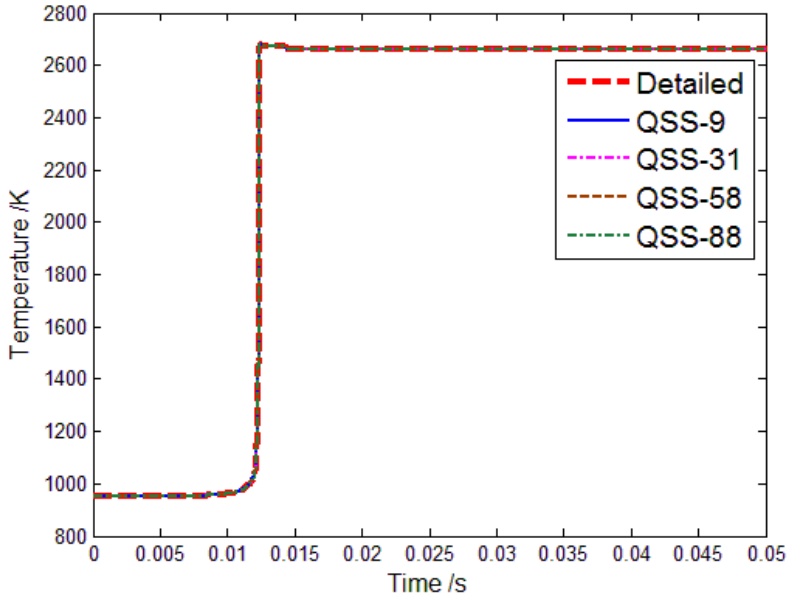

Figure 12 n-pentane carbon net flux

Since the GRI $NO_x$ mechanism is compact with only about three to five QSS species potential candidates, we focused on carbon reaction network and the carbon net fluxes to choose QSS species, while leaving the $NO_x$ mechanism to the on-the-fly reduction. By applying different values of threshold on the maximum net fluxes, possible global QSS species were selected in four groups and listed in Table 4. The species with different maximum net carbon fluxes were ranked in ascending order. Four groups with 9, 31, 58, and 88 QSS species were selected according to different threshold applied.

| Max net flux threshold | Number of QSS species |
|---|---|
| $10^{-6}$ | 9 |
| $10^{-4}$ | 31 |
| $10^{-3}$ | 58 |
| $10^{-2}$ | 88 |

Table 4 QSS species selection for n-pentane

Subsequently, up to 88 possible QSS species were selected and verified in PFR simulations using the hybrid reduction. The same initial temperature, pressure and the fuel/air mixture equivalence ratio of 1.0 were used this time. The flux cutoff value was set as 99.9% in the hybrid reduction scheme. The results for the temperature and mass fractions are shown in Figure 13. .



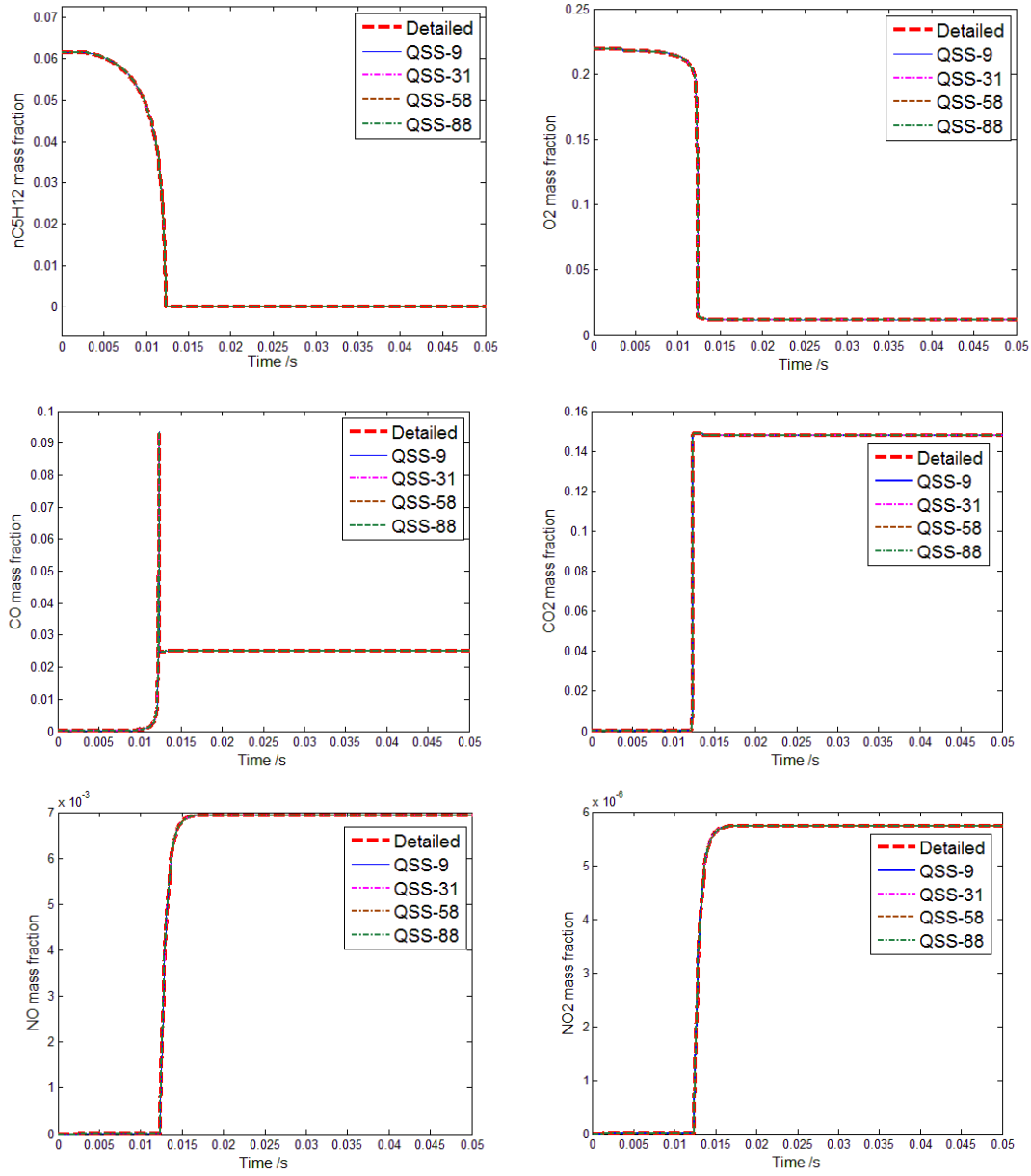



Figure 13 Temperature and species profile for n-pentane in PFR

Good agreement has been achieved between results of four QSS species selections and the detailed simulation. The major combustion characteristics have been captured successfully. Over one fifth of total species were reduced by QSSA globally from the n-pentane-nox mechanism, and non-QSS species were further reduced dynamically by the on-the-fly reduction.

As a result, four groups of QSS species were validated in PFR, which demonstrates

the capability of the hybrid reduction for maintaining the accuracy while reducing the size of n-pentane mechanism.

### 4.1.2 Hybrid reduction of n-pentane in KIVA-3V

In the next step, the selected QSS species were used in the hybrid reduction scheme in the multi-dimensional engine CFD simulations. The KIVA-3V and CHEMKIN codes were modified to allow the calculations with larger mechanisms. The detailed introduction of KIVA-3V's computational framework can been seen in our previous work (He, Androulakis, et al., 2010a). In brief, a HCCI engine with the piston at bottom dead center (BDC) is represented by a 2D axial symmetric mesh with 1052 computational cells (Figure 14). The hybrid reduction is integrated in chemistry calculations at each computational cell at each time step (Zhang et al., 2013). The transport calculations only involve non-QSS species after chemistry calculations during each loop, which is similar as the framework illustrated in previous Figure 1.

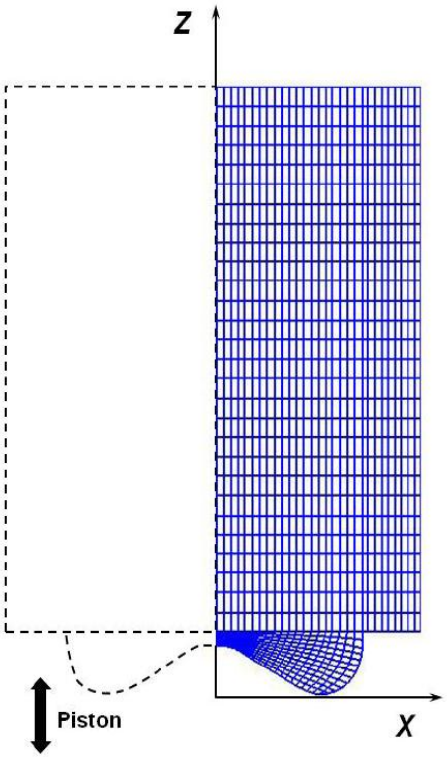



Figure 14 HCCI engine in KIVA-3V

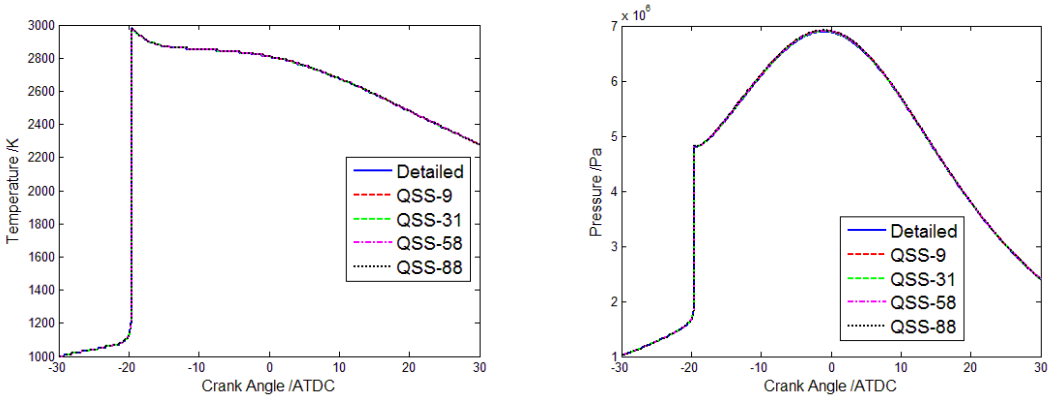
The engine piston's parameters and conditions are listed in Table 5. The crank angle after top dead center (ATDC) in the simulation starts from -30.0° to 30.0°, covering the period of piston moving toward and then away from the top dead center (TDC). The fuel/air mixture equivalence ratio was set as 1.0 at chemical stoichiometric ratio. The flux cutoff value was still 99.9% in the hybrid reduction. Four different engine speeds from 900 rpm to 1800 rpm were used in the demonstration.

| **Engine Parameter** | **Value** |
|---|---|
| **Bore diameter (cm)** | 13.716 |
| **Stroke (cm)** | 16.51 |
| **Compression ratio** | 16:1 |

| | |
|---|---|
| **Engine speed (rpm)** | 900, 1200, 1500, 1800 |
| **Initial temperature (K)** | 1000 |
| **Initial pressure (MPa)** | 1.0 |
| **Equivalence ratio** | 1.0 |
| **Crank angle range (ATDC)** | -30° ~ 30° |

Table 5 Engine parameters for HCCI engine in KIVA-3V

Firstly, we compared the hybrid reduction results of four QSS species groups with the detailed mechanism simulation at the engine speed 900 rpm. In Figure 15, the ignition delay time obtained from four QSS species groups coincide with the detailed simulation result in the temperature and pressure profiles. The mass profiles of major species are also in good agreement with the detailed simulation. It indicates that the QSS species selections up to 88 species are appropriate and able to produce accurate results in the hybrid reduction.



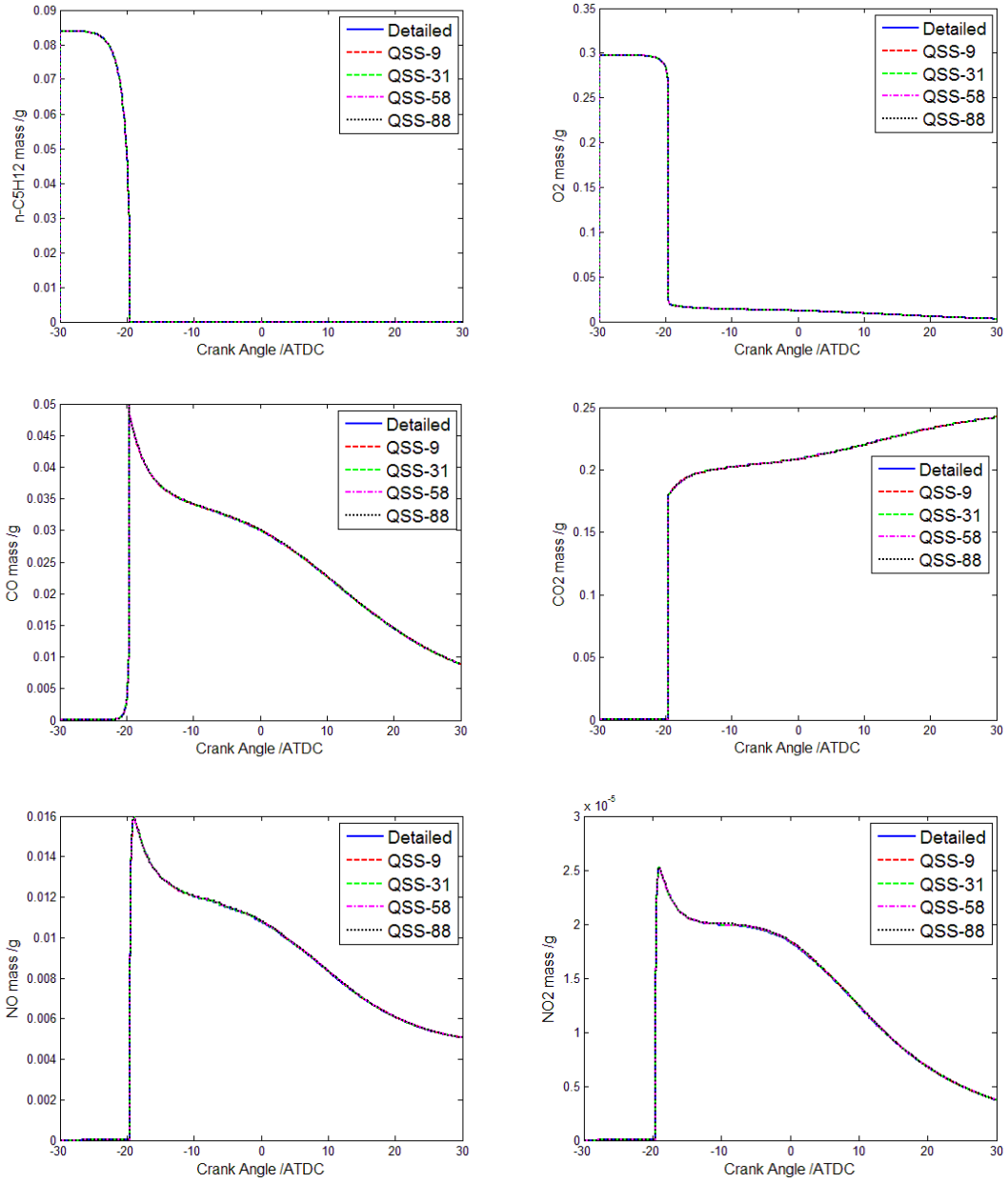



Figure 15 Profiles at 900rpm for n-pentane in KIVA-3V

Then the QSS species selection with 88 species was used in the hybrid reduction under different engine speeds, and was compared with the detailed simulations. As shown in Figure 16, the temperature and pressure profiles suggest that the hybrid reduction results agree with the detailed simulation results at 900 and 1200 rpm, but have larger errors at higher engine speeds. With more QSS species selected, larger

errors in hybrid reduction scheme occur when reaction conditions are far from conditions where QSS species are selected, which is due to the global reduction by QSSA. At higher engine speed like 1800 rpm, the kinetic processes that govern ignition become slower relative to the movement of piston, which means less time for the chemical reactions. By assuming 88 QSS species globally, we simplified the reaction network and altered the reacting pathways. The extent of reactions and heat might be larger than the detailed reaction networks in some computational cells.

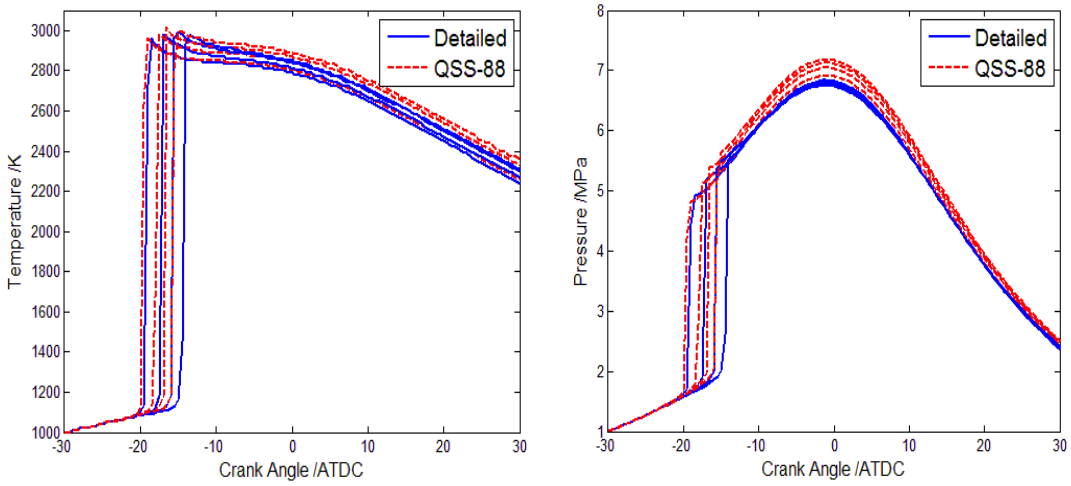
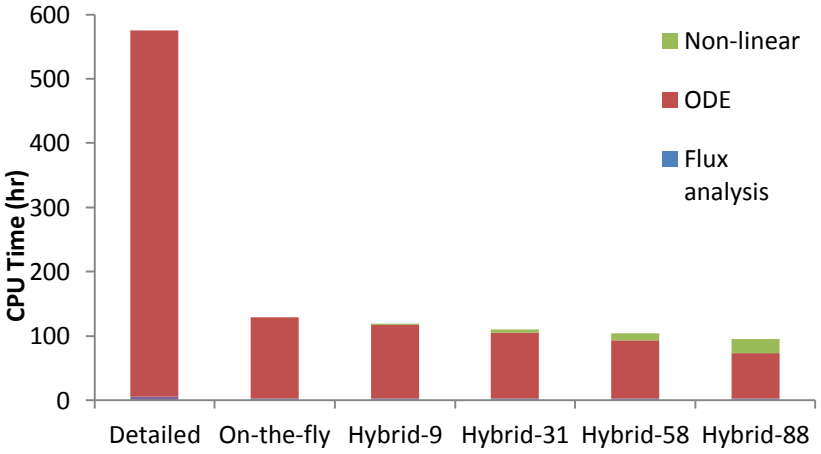



Figure 16 Temperature and pressure for QSS-88 of n-pentane at 4 speeds in KIVA-3V

As shown in Figure 17, the CPU time analysis indicated the significant time saving by the hybrid reduction scheme. The workstation for the simulation is Dell T7500. Compared with the detailed simulation, the CPU time reduced from over 570 hours to less than 130 hours, which is mainly due to the on-the-fly reduction. By magnifying the CPU time profile, it can be seen that the total time is also decreasing when more QSS species are selected. More QSS species will increase the time in non-linear algebraic solver, but further reduces the total time. The reason is that the ODE

system is more complicated and needs more time to be solved than non-linear algebraic equations. With more QSS species selected, there are less non-QSS species left for the on-the-fly reduction and less complexity in the ODE system.

The time for transport calculation is small and the saving is not obvious. The reason is that the HCCI model in KIVA is simple and requires much shorter CPU time. Therefore, more complex models will be investigated in the future to investigate the time saving feature of the hybrid reduction. The hybrid reduction is expected to play a more important role for larger detailed mechanisms like n-pentane in engine CFD simulations.



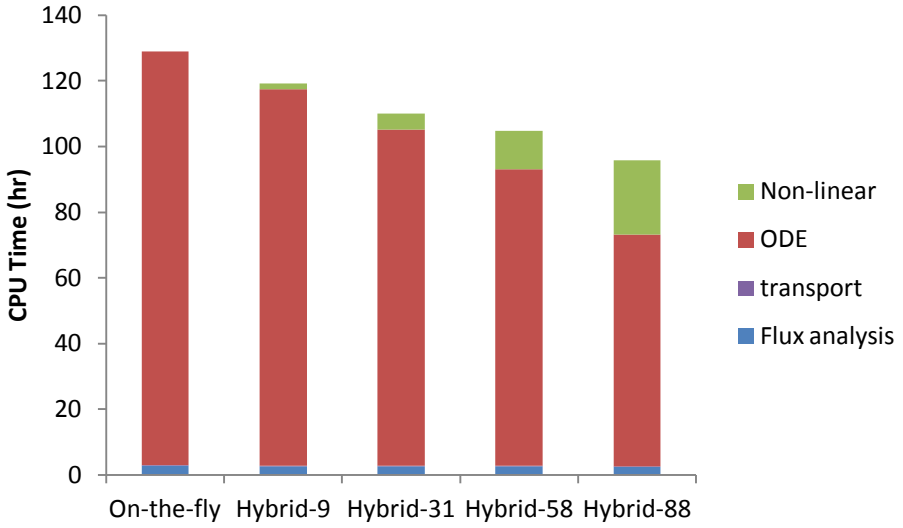



Figure 17 CPU time analysis for n-pentane in KIVA-3V

### 4.2 Demonstration with methyl butanoate (MB) mechanism

Methyl butanoate (MB) is an important biodiesel surrogate mechanism proposed by Fisher et al (Fisher et al., 2000). It contains an ester group and a shorter carbon chain compared with other complex typical biodiesel surrogates. Although it has some negative issues in the simulation such as its weak negative temperature coefficient (NTC) behavior, it is still used commonly in many combustion and engine simulations.

With the experience on n-pentane, we further extended the hybrid reduction scheme to methyl butanoate (MB) with the $NO_x$ sub-mechanism. The mechanism now has 278 species and 1272 reactions.

4.2.1 QSS species selection for methyl butanoate (MB)

Similarly, only the net carbon fluxes for all species were calculated in adiabatic PFR for simplicity. The initial conditions were similar with those for n-pentane, with the initial temperature 1050K, pressure 9.6atm, and the stoichiometric ratio for fuel/air mixtures. The nitrogen reaction network was maintained during the QSS species selection, waiting for the later on-the-fly reduction.

The maximum value of net fluxes throughout the simulation is obtained in Figure 18.

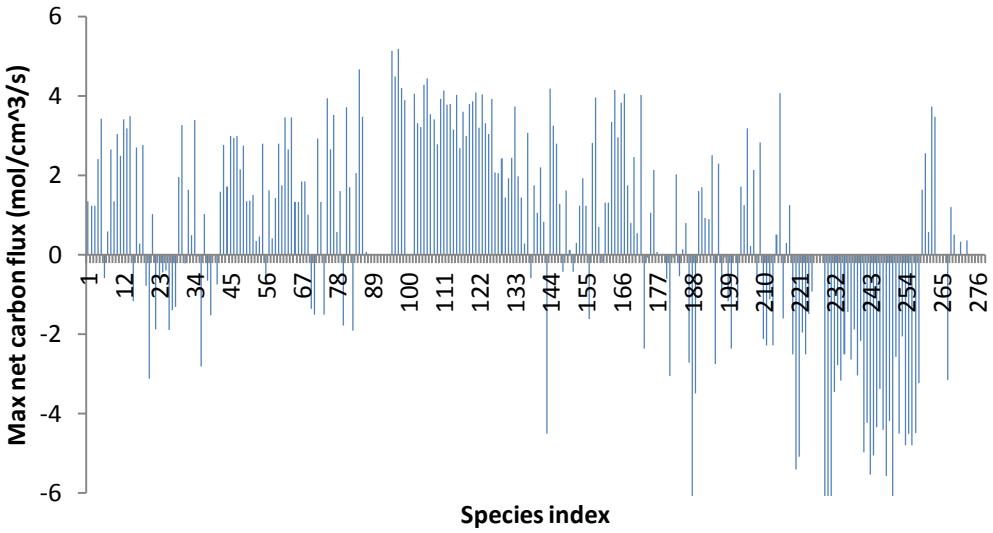


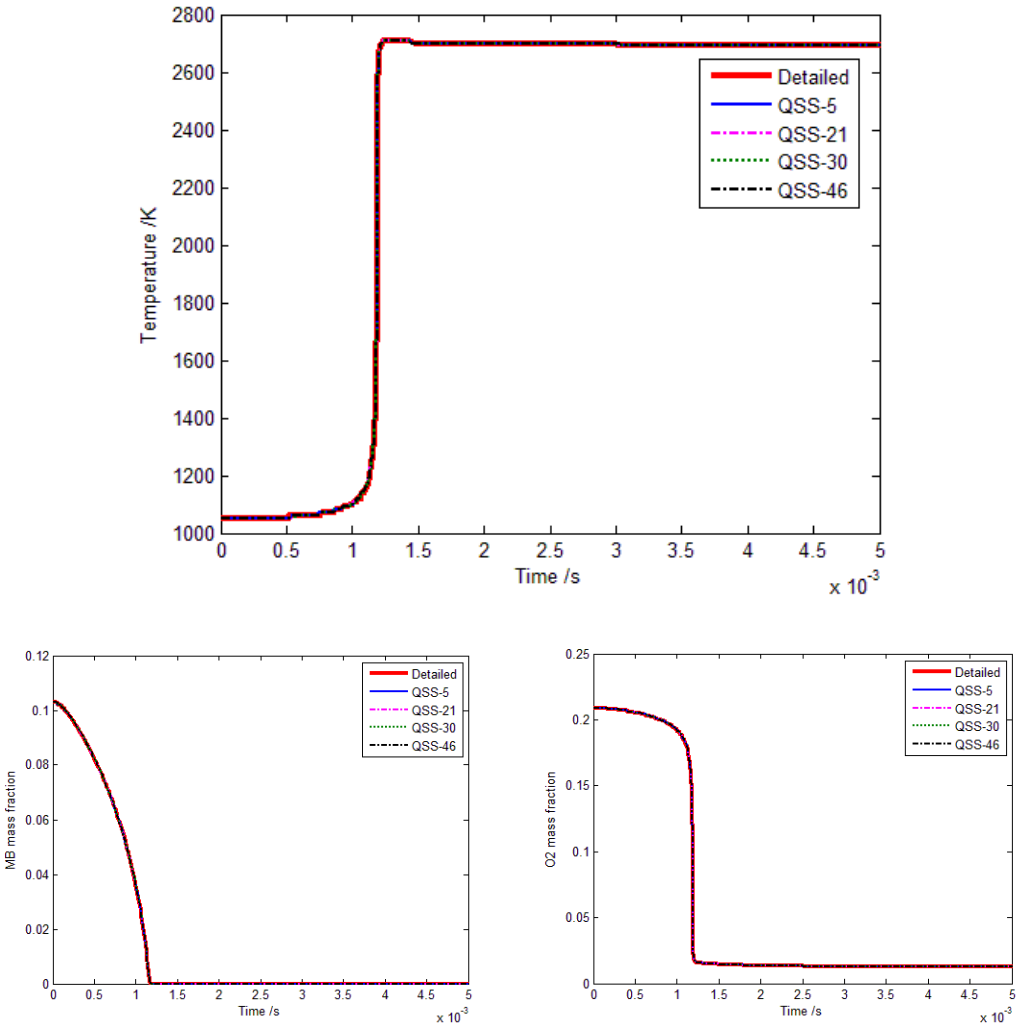

Figure 18 MB carbon net flux

The species with small maximum net flux values were sorted in ascending order. Four groups of QSS species candidates were selected according to different threshold applied. Then, the 5, 21, 30 and 46 QSS species selections were used as the global QSS species in PFR simulations for the validation purpose.

| Max net flux threshold | Number of QSS species |
|---|---|
| $10^{-6}$ | 5 |
| $10^{-4}$ | 21 |
| $10^{-3}$ | 30 |
| $10^{-2}$ | 46 |

Table 6 QSS species selection for pentane

The results of temperature and mass fractions of major species were shown and compared with the detailed simulation results in Figure 19.



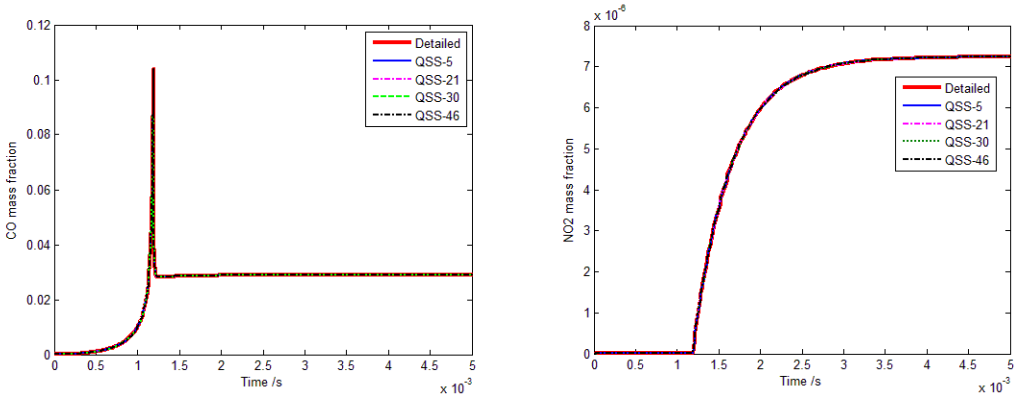



Figure 19 Temperature and species profiles for MB in PFR

Again, the results showed a good agreement for all QSS species selections, indicating up to 46 species were suitable QSS species in the hybrid reduction.

### 4.2.2 Hybrid reduction of methyl butanoate (MB) in KIVA-3V

Four groups of QSS species were then tested in KIVA-3V to further investigate the performance of QSS species selections and to apply the hybrid reduction in the engine CFD simulations. The engine piston simulations were conducted from crank angle -30.0° to 30.0° ATDC, using the same initial conditions as in Table 5. The value of flux cutoff was 99.9% in the hybrid reduction.

The results of temperature, pressure and mass fractions of major species are shown in Figure 20. Four groups of QSS selections were compared with the detailed mechanism simulations.

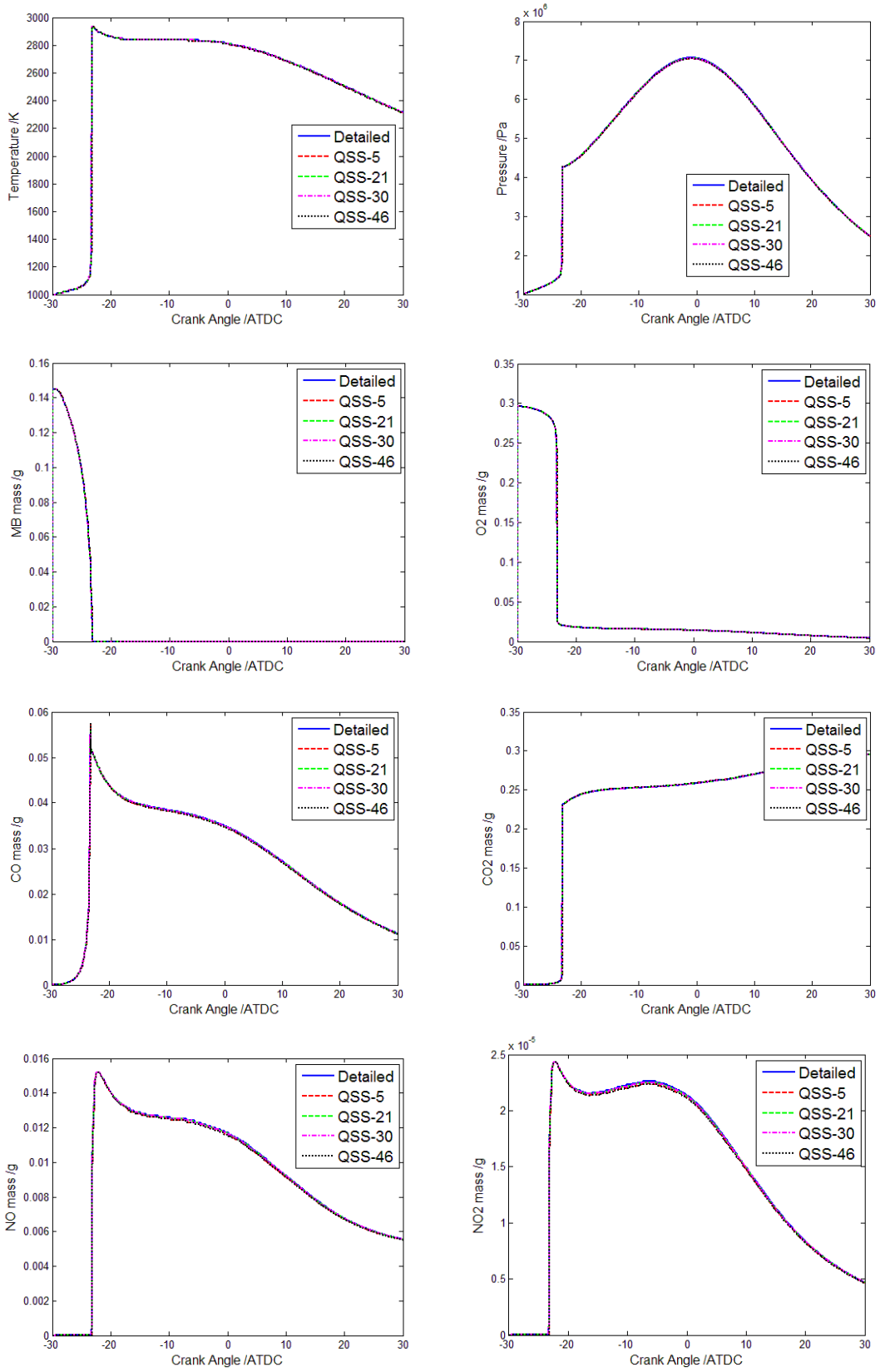



Figure 20 Profiles for MB at 900rpm in KIVA-3V

The results showed a good agreement between all QSS species selections and the

detailed mechanism simulation at engine speed 900rpm. This indicated that 46 selected species were good QSS species in the hybrid reduction scheme and did not alter the combustion chemistry significantly.

The 46 QSS species were used and further demonstrated the hybrid reduction of MB under different engine conditions in Figure 21. The temperature and pressure profiles were predicted accurately for 900 and 1200rpm in comparison with the results of the detailed mechanism simulation.

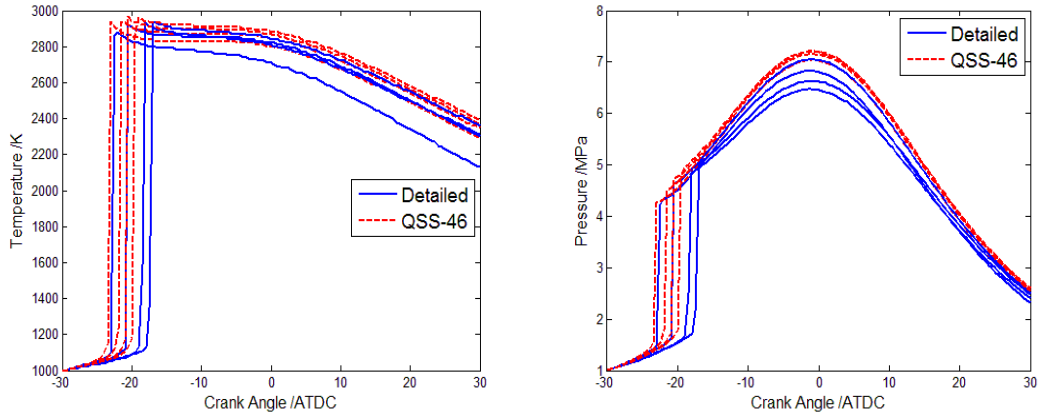



Figure 21 Temperature and pressure for MB at 4 speeds in KIVA-3V

The CPU time in KIVA was summarized in Figure 22. Over 70% CPU time savings in total was achieved after using the on-the-fly reduction, and slightly more savings by applying QSSA in the hybrid reduction. The cost of chemistry calculation decreased slightly with more QSS species selected for 5, 21 and 30 QSS species selections. However, we could also observe that the time savings for ODEs cannot compensate the additional cost to solve algebraic equations for 46 QSS species. The increased time in total might be resulted from the mathematical stiffness introduced by the QSSA, and need to be further investigated.

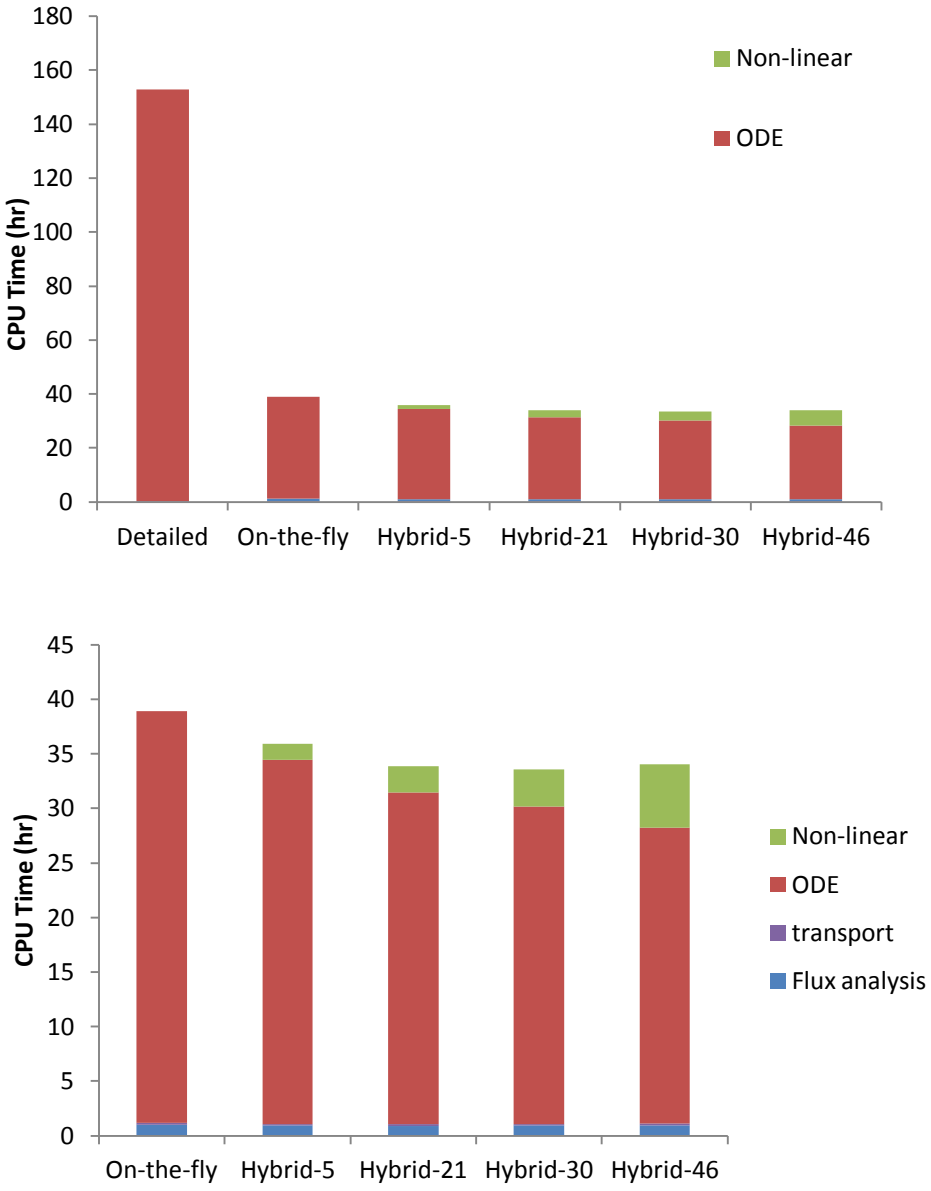



Figure 22 CPU time analysis for MB in KIVA-3V

## 4.3 Conclusions

In this chapter, the hybrid reduction framework has been applied successfully on n-pentane and MB mechanisms in both PFR and KIVA simulations. The flux-based QSS species selection recognized QSS species candidates appropriately, and then PFR

simulations quickly verified those QSS selections. The relevant data for QSS species selections of n-pentane and MB biodiesel surrogate was obtained. The threshold of $10^{-2}$ mol/(cm$^3$ · s) is appropriate for the maximum net flux of most species during the quick selection. For both n-pentane and MB, the hybrid reduction scheme demonstrated its capabilities to predict the combustion characteristics accurately and to save the computational cost significantly in engine simulations in KIVA. In general, the CPU time is reduced as more QSS species are selected. The savings on ODE calculations will compensate the additional cost for non-linear algebraic equations. The overall results suggest that the hybrid reduction scheme is a powerful tool for detailed CFD simulations, especially for larger chemical mechanisms. The future study will employ more complex transport models and huge mechanisms like methyl decanoate (MD) with thousands of species and over ten thousand reactions.

# Chapter 5

# Conclusions and Future Perspectives

## 5.1 Conclusions

In this thesis, we first established the computational framework in CRUNCH CFD® based on the previously developed hybrid mechanism reduction scheme. The framework has been fully tested and demonstrated stepwise using hydrogen and methane detailed mechanisms. With the hybrid reduction scheme, detailed mechanism has been incorporated in the zero-dimensional PFR combustion simulation and 2D $CH_4/O_2$ hypersonic injector combustion. The computational costs were also evaluated and compared between the detailed simulation and the simulation using hybrid reduction. The hybrid mechanism reduction scheme reduced the calculation time in CRUNCH CFD®, while maintaining the high accuracy. The selection of QSS species for methane in the hybrid reduction was also based on the fast identification using the maximum net element flux, and the results indicated its efficiency and accuracy. This work provides important insight for incorporation of detailed kinetic models in computational combustion studies, and lay the foundation for our future work on reactive flow simulations.

In the latter part, we also extended the hybrid reduction scheme together with fast QSS identification method to larger reaction mechanisms. The demonstration results of PFR model and HCCI engine CFD simulations showed the selected QSS species

were appropriate and in accordance with our expectation. The combined technique of hybrid reduction scheme and fast QSS selection method is efficient to perform complex combustion simulations with transport intensive applications and with large detailed mechanisms.

## 5.2 Suggestions for future work

Much efforts are still required for the applications of the hybrid mechanism reduction in the future development. The hybrid reduction scheme established in CRUNCH CFD® enabled more complex combustion simulations, so one interest will be simulate combustions using detailed mechanisms with more complex transport models. Studies are also needed about those factors that affect the computational costs in the hybrid reduction scheme in CRUNCH CFD® as well as the stiffness of the chemical kinetics system when large numbers of QSS species are introduced. The coding algorithm and matrix operations may be further simplified and optimized. The human-machine interface (HMI) can be more user friendly and efficient.

For larger mechanisms like biodiesel surrogates, a more effective approach is required to implement the fast QSS species selection into the framework, so that no prior detailed run is needed any more to obtain the maximum net element flux.

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