

A Two-stage Reduction for Complex Combustion Chemistry

By

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ABSTRACT OF THE THESIS

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The combustion of hydrocarbon is a main energy resource for transportation. It is easy to start but very hard to understand and simulate. There have been several efforts to build detailed kinetic mechanisms from elementary reactions. Although they are highly accurate and well capture the complicated chemistry of combustion process, it is expensive to model with detailed mechanisms because their size is too large. Furthermore, it is not effective to apply detailed mechanism while there are only some of species and reactions involved in a typical condition. Therefore, a suitable reduced mechanism for such considered condition is a hot requirement. Recently, Petzold et al., and Androulakis suggested an automatic mechanism reduction based on the mathematical programming method. Following their approach, Banerjee et al. applied GA search to generate reduced mechanisms. The fruit of that work is a reduced mechanism library, which can govern combustion of air – methane mixture with high accuracy. Nevertheless, the GA reduction method is hard to directly apply to the complex chemistry whose solution space is large. It, therefore, needs a first step of reduction,

which can condense the search space of complex combustion mechanisms. Androulakis provided a method based on flux analysis to build a reduced mechanism with a suitable cut-off value of element flux accumulation. Although his method is flexible and very fast, the obtained mechanism can contain some species, which can be further eliminated. In this work, the two approaches mentioned above were combined to form a two-step reduction procedure on n-pentane and n-heptane mechanism. The flux analysis reduction was used first to obtain a skeleton reduced mechanism. Then the GA reduction considered the obtained mechanism as a detailed mechanism for parallel GA search. Nine conditions of n-pentane and nine conditions of n-heptane oxidation were investigated. Although the size of the final reduced mechanisms is much smaller than that of detailed mechanisms, they well estimate the oxidation process.

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Chapter I

INTRODUCTION

Hydrocarbon combustion, a main energy resource for transportation, has been used for nearly a century. However, it is not easy to understand and simulate because the chemistry of fuel combustion is too complicated with hundred of species and thousand of reactions which occur, develop, and disappear in very short time. In the past few decades, there have been several efforts to catch up the chemistry of hydrocarbon combustion phenomenon. Several detailed kinetic mechanisms, which are combinations of elementary reactions, have been constructed manually or computationally to serve a wide range of oxidation condition. They present a whole picture of combustion process with so many chemistry channels co-exist. Detailed mechanisms of hydrocarbon oxidation, the fruits of these endless efforts can be found in an excellent review written by John M Simmie (2003). Although they can help to estimate the complexity of combustion process with great accuracy, detailed mechanisms bring many disadvantages. First of all, the size of a detailed mechanism is too large. Sometime, it contains hundred of species and thousand of reactions. It takes much time to simulate combustion with detailed mechanism. Second, although detailed mechanism governs combustion process at huge range of condition, there are only some species and reactions involved in a typical condition. Therefore, it raises a call for a suitable mechanism method in order to find a suitable reduced mechanism for such situation.

Several chemists have been trying to develop reduction methods for the aim of dimension elimination. Most of these approaches base on a time-scale and can be found

in a review written by Tomlin *et al.* (1997). The oldest and also simplest method is quasi-steady state approximation (QSSA), first developed by Peter (1987). Under the assumption that some certain species are at steady state and some reactions are partially equilibrium during combustion process, QSSA removes these species and reactions from detailed mechanism to obtain a reduced mechanism. The validity of the supposed hypotheses on quasi-steady state species and partial equilibrium reactions is based on the chemistry knowledge of users. QSSA method, therefore, can potentially create a huge error. Furthermore, it is not a fully automatic method. Tools were subsequently developed to overcome the QSSA limitations. J-Y Chen (1997) presented a computer aid reduction method (CARM) source code for automatically generating a reduced mechanism. CARM defines quasi-steady state species by analyzing first order sensitive coefficients then decouples them from detailed mechanism. Simple, and easy to use, CARM has been applied in many problems. Lam and Goussis (1994) presented a computational singular perturbation method (CSP) using a transformation of system basis vectors for selecting steady-state species and equilibrium reactions. However, the CSP was developed on linear relationships. As a result, the subset of ODEs coming from CSP changes with time and cannot be written down as explicit equations.

Maas and Pope (1992) suggested another reduction technique named intrinsic low-dimension manifold (ILDM), which overcomes the disadvantages of QSSA. Based on eigenvalue analysis, ILDM defines fast factors by comparing their eigenvalue to the reverse of time scale of the flow and removes them from a detailed mechanism to form reduced mechanisms. With input as a detailed mechanism and the degree of model freedom, ILDM tabulates chemistry quantities, for example reaction rates, on low

dimension manifold for later use. ILDM works automatically and is a far successful comparing to QSSA and CARM. However, it is a complicated algorithm. Like CARM, CSP, and QSSR, the reduced mechanism found by ILDM is not explicit. Furthermore, when the degree of model freedom is not appropriate, ILDM may give ill solutions (András Büki *et al.* (2002)).

Another reduction technique presented by Pope (1997) is “in situ adaptive tabulation” method (ISAT), which builds a reaction mapping by solving linearly independent ODEs resulted from detailed mechanisms at the first step. The map is then stored in a binary data structure tree. The value of a new point in the next calculation is interpolated from that of nearby points in the tree. If the distance from this point to other points in the tree is far, ISAT will integrate and store the result in the tree for updating. ISAT is widely applied on computational chemistry. It has been used in not only homogeneous but also heterogeneous environment (Mazumder *et al.* (2005), Hedengren *et al.* (2005)). However, it does not still give out any explicit reduced mechanism.

Lu *et al.* (2006) recommended a new reduction method named directed relation graph (DRG). The idea behind DRG is to define unimportant species and reactions through analyzing the effect of eliminating a species to the production rate of the others. Based on the analysis, DRG builds a relation graph of immediate correlative error among species in a detailed mechanism. Thus, by removing branches, which have error smaller than a given threshold, users obtain a reduced mechanism. The main advantage of DRG is that it can automatically generate an explicit skeleton mechanism from a detailed mechanism. Nonetheless, the complexity of this algorithm is quite high.

Recently, Androulakis (2004) provided a novel method for mechanism reduction based on the analysis of element flux. This approach uses a time-integrated pointer to record the element transformations during simulation. The element flux reveals not only the element transformation in detailed mechanism but also the relationship among species. Additionally, the accumulation element flux of each species shows an element transformation network of detailed mechanism like a water pipe system in a city. The species, which have big accumulated element flux, are assumed unimportant because there is only a small amount of involved element. Thus, users can remove these species to form a skeleton mechanism without affecting accuracy. This method presents many advantages. It is very fast and highly flexible as well as powerful, especially when the detailed mechanism is large such as n-pentane or n-heptane. By integrating detailed mechanism once, users can gain many reduced models with different sizes by changing the cut-off value. These reduced mechanisms are explicit and can serve various purposes. Furthermore, as a byproduct, the element transformation network reveals the reaction pathways of the considered mechanism.

Banerjee *et al.* (2003) suggested an automatic mechanism reduction based on the mathematical programming approach developed by Petzold *et al.* (1999) and Androulakis (2000). This method tries to automatically find a subset of species and reactions from a detailed mechanism with acceptable error in predicting profiles of some given factors such as species and temperature. Similar to the flux analysis method, the mathematical programming approach assumes the detailed mechanism is known with high accuracy. Then, the mathematical programming scheme solves an optimization problem where a set of minimum number of species – reduced mechanism – is found with a given accuracy

constraint. This technique can overcome the disadvantages of other methods such as ISAT, CARM, and ILDM mentioned above. First of all, it overcomes the memory shortage since the reduced mechanism is explicit. Once generated, it can be served several times. Next, it is very flexible. Depending accuracy given by users, the method can generate different reduced mechanisms. Furthermore, the explicit reduced mechanisms make way for building a library of reduced mechanisms for adaptive chemistry. In addition, it can estimate itself the error of reduced mechanisms.

Although mathematical programming technique scheme does indeed give rise to accurate and flexible reduced models, but is itself an expensive operation since it requires multiple integrations of the stiff, nonlinear ODEs describing the kinetic source term. Also, the number of binary variables handled by the Mixed Integer Nonlinear Programming (MINLP) formulation can be restrictive. Thus, direct application of this procedure in very large mechanisms may prove to be inefficient. For such cases it is found to be efficient to use a two-stage reduction procedure, where a first level reduction can be done by flux-analysis, followed by a more detailed reduction using the integer programming approach.

In this work, we shall show the work of two-step reduction approach on n-C₅H₁₂, and n-C₇H₁₆ combustion mechanism. The flux analysis was used first to achieve skeleton mechanisms from the detailed mechanism of n-pentane (385 species and 1895 reactions) and n-heptane (561 species and 2539 reactions) of Curran *et al.* (1998a). By setting a suitable cut-off threshold of accumulated element flux for n-pentane and n-heptane mechanism reduction, we obtained Flux-reduced mechanisms for 18 distinctive oxidation conditions (nine for each kind of considered fuel). The flux reduction

eliminated at least 50% number of species and indirectly disabled 50% number of reactions. These skeleton reduced mechanisms were further trimmed by GA reduction. Since the size of these flux-reduced mechanisms is still large, sometimes they contain hundreds of species and thousands of reactions; a parallel GA reduced procedure was applied to speed up the calculation. The largest final reduced mechanism is at low temperature oxidation. It contains 100 species and 470 reactions for n-pentane and 180 species and 790 reactions for n-heptane. The smallest reduced mechanism is at high temperature oxidation. It consists of 40 species and 135 reaction for n-pentane and 103 species and 477 reactions for n-heptane. Although the size of the final reduced mechanisms is very much smaller than that of the original detailed mechanism, they capture the complicated chemistry of combustion with great accuracy. These reduced mechanisms are explicit. They can therefore serve several times. Furthermore, all kinetic parameters of reduced mechanisms come from the original detailed mechanisms. They are not adjusted as in the work of Su *et al.* (2005). We observe the high temperature chemistry in fuel rich mixture oxidation of n-pentane even though at low temperature. It becomes dominant in NTC of fuel rich mixture oxidation. The high temperature chemistry channels also occur in n-heptane fuel rich mixture oxidation at NTC. However, these channels are not as strong as they are in the case of n-pentane. The low temperature chemistry channels appear in stoichiometric and fuel lean mixture oxidation at NTC of n-pentane. These channels are ascendant in fuel lean mixture oxidation. The low temperature chemistry channels show up in stoichiometric and fuel lean mixture oxidation of n-heptane at NTC as well. Nevertheless, these channels are not as powerful as they are in n-pentane.

The thesis is constructed as following. After introduction, chapter 2 details the two-state reduction approach. The basic ideas of the two-state reduction method are displayed first in this section. Then, the framework of parallel GA reduction is followed. The reduced mechanisms of nC₅H₁₂ and n-C₇H₁₆ at different conditions as well as the reaction pathways that characterize the combustion process of such oxidation conditions are presented in chapter 3. Finally, the last chapter summaries the work and presents some ideas of the future work.

Chapter II

TWO-STEP MECHANISM REDUCTION

A methodology is developed to automatically construct reduced mechanisms for the aim to minimize the dimension of the system while retaining sufficient accuracy in the prediction of specific species profiles. We will describe the two-state reduction procedure in this section by combining the flux analysis and mathematical programming method. In this section, the fundamental of flux analysis is illustrated first, followed by the basis ideas of the mathematical programming approach.

2.1. Flux analysis

The concept of element flux analysis introduced by Revel *et al.* (1994) allows one to develop time-dependent flux diagrams that identify key reaction pathways with minimal effort. The main idea is to study principal reaction pathways along the reaction process coordinate. The atomic fluxes for each atom (C, H, O, N, Cl, S) at different reaction times are calculated, based on reaction rates, and the major sources and sinks for each element are identified. The instantaneous chemical flux of atom A from species j to species k through reaction i is accordingly defined as:

$$A_{ijk} = q_i \frac{n_{A,j} n_{A,k}}{N_{A,i}} \quad (1)$$

where q_i is the net production rate of reaction i (mol s^{-1}), $n_{A,j}$ is the number of atoms A in species j, $n_{A,k}$ is the number of atoms A in species k, and $N_{A,i}$ is the total number of atoms

of element A in reaction i. For any given atom (A), we can then consider the transformations that occur from species to species by all reactions in the network. Hence, the total mass transformation of element A for any pair of species, which have the reaction-product relationship in a reaction, can be defined by

$$\bar{A}_{FROM,TO}(t) = \sum_{i=1}^{N_R} A_{i,FROM,TO}(t) \quad (2)$$

The fluxes defined in Eq. 1, and 2 are functions of time. Therefore, one repeats the analysis at pre-selected time instances during the reaction process. Androulakis (2004) suggested the concept of a time-integrated flux indicator to overcome this limitation. The main idea is to derive (over time) an indicator for a source-sink combination based on integration of the quantity defined in Eq. 2. The quantity is then subsequently normalized as a mean for representing the results in a unified way. Therefore, the following quantity is used:

$$\hat{A}_{FROM,TO}(t) = \frac{\int_{t=0}^{\tau} \bar{A}_{FROM,TO}(t) dt}{\max \int_{t=0}^{\tau} \bar{A}_{FROM,TO}(t) dt} \quad (3)$$

The integrals in Eq. 3 are estimated numerically by taking into account all time instances as the integrator is generating them. In this way, the entire reaction trajectory is taken into account, and there is no need to a priori select the location of the snapshots. Moreover, the quantity defined in Eq. 3 allows one to assign a unique number to each source-sink pair, which is representative of the entire reaction period. The normalization as defined in

Eq. 3 ensures that pathways activated at different points in time receive appropriate weighting.

Time-integrated element flux analysis examines the values of the quantities defined in Eq. 3 and allows one to characterize the transformations that take place during the reaction period. The analysis of flux transformation reveals key pathways in terms of source-sink relationships. However, this analysis does not reveal any information related to the ways, the specific reaction paths, that these transformations take place. The purpose of the time integrated element flux analysis is to establish “*global*” insight into the reaction pathways. It allows for a comprehensive and macroscopic view of the reactant transformation to intermediate(s) and finally to products. By removing the temporal dependency it makes possible to establish these types of relationship. The results for this analysis for pentane oxidation are shown in figure 1 where it can be seen that in fuel rich conditions the flux towards decomposition reactions is higher.

The flux analysis can reveal the element flux transformation and establishes a network among species in any mechanism. For a given pair of source-sink species in that network, we define the strength of the connection between them as the reciprocal of the accumulation of normalized element fluxes. The role of a species is weighed from the strength of its connections to the others. A species having large accumulation of element flux is unimportant because the amount of mass transferring to that species is small. As a result, it can be removed from the detailed mechanism without much affecting the accuracy to form a “skeleton” mechanism.

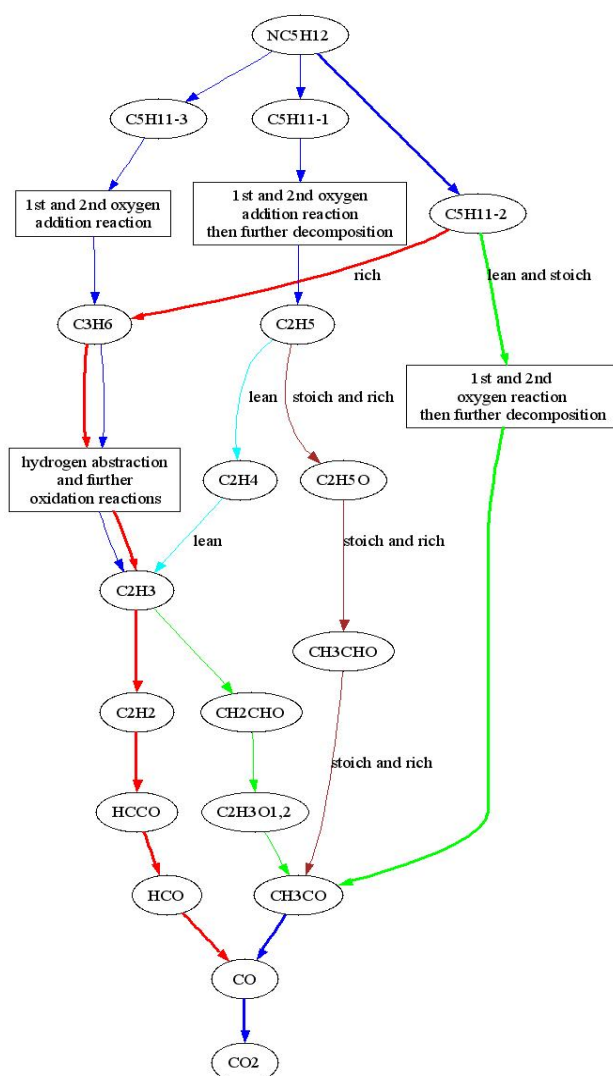


Figure 1: Main pathways in pentane oxidation. As it shows fuel rich conditions exhibit higher fluxes through fuel decomposition pathways compared to oxygen addition reactions that are more prevalent in fuel lean conditions.

2.2. Mathematical programming

The mathematical programming approach, presented by Androulakis (2000) and adapted by Banerjee *et al.* (2003), assumes that the considered detailed mechanism is known with a high accuracy. So that, the aim of mathematical mechanism reduction is to find the subset of species and reactions which can characterize the reaction process while retaining the expected accuracy to compare to that of detailed mechanism. Thus, it raises an optimization problem in which the objective function is to minimize the number of species and reactions with constrain is the desired accuracy of some important factor profiles predicted by the reduced model. This optimization problem for an isobaric batch reactor can be defined as follows:

$$\mathfrak{J} = \min_{\lambda \in g^N} \sum_{i=1}^{N_s} \lambda_i \quad (4)$$

Subject to

$$\theta = \left(\sum_{j \in \Omega} \int_0^\tau \left(\frac{y_j^{red} - y_j^{det}}{y_j^{det}} \right)^2 d\tau + \int_0^\tau \left(\frac{T^{red} - T^{det}}{T^{det}} \right)^2 d\tau \right)^{1/2} \leq \varepsilon \quad (5)$$

$$\frac{dy_j^{red}(\tau)}{d\tau} = \frac{R_j M_j}{\rho}, j = 1, \dots, N_s \quad (6)$$

$$\frac{dT(\tau)}{d\tau} = - \sum_{j=1}^{N_s} \frac{R_j M_j h_j}{\rho \bar{C}_p} \quad (7)$$

$$R_j = \sum_{i=1}^{N_r} \prod_{j=1}^{N_s} \langle \lambda_j \rangle_i \left(\nu_{j_i}^{rev} - \nu_{j_i}^{forw} \right) q_i \quad (8)$$

$$q_i = \kappa_{forw_i} \prod_{j=1}^{N_s} X_i^{\nu_{ji}^{forw}} - \kappa_{rev_i} \prod_{j=1}^{N_s} X_i^{\nu_{ji}^{rev}} \quad (9)$$

$$\kappa_{forw_i} = K_{forw_i} T^{\beta_i} e^{-\frac{E_{forw_i}}{RT}} \quad (10)$$

$$\kappa_{rev_i} = K_{rev_i} T^{\beta_i} e^{-\frac{E_{rev_i}}{RT}} \quad (11)$$

$$\langle \lambda_j \rangle_i = \begin{cases} 1 & \text{if species } j^{\text{th}} \text{ participates in reaction } i^{\text{th}} \\ 0 & \text{if not} \end{cases}$$

Here λ_i in equation 4 stands for the presence of the species i^{th} in a reduced mechanism and is a binary variable. Its value is 0 if the species is removed or 1 if that species is in the reduced mechanism. The subjective function \mathfrak{S} represents the number of species in a reduced mechanism. The accuracy of the reduced mechanism is determined by users through (ϵ) . The error, θ calculated in equation 5, of a reduced mechanism is the estimation error of the contour of user-defined key factors in considering period of time. y_j^{red} and y_j^{det} represent for mass fraction of a species in a reduced mechanism and detailed mechanism respectively. T^{red} and T^{det} are temperature of reduced mechanism and detailed mechanism respectively. Equation 6 and 7 are mass and heat conservation of a model. Whereas equation 8 characterizes the net rate of production formation for species j^{th} measured by the difference of reverse and forward reaction rate in the involving

elementary reactions. $\nu_{j_i}^{rev}$ and $\nu_{j_i}^{forw}$ are stoichiometric coefficient of species j in reaction i . q_i in equation 9 denotes the intrinsic rate of individual reaction, which is governed by the modified Arrhenius law as depicted in equation 10 and 11.

In the reduction process, whenever a species is removed from a detailed mechanism, the reactions involving this species are also removed from the system, that is to set $\langle \lambda_j \rangle_i$ equal to 0. Therefore, by decoupling species, one indirectly reduces the number of reactions. The solution of (4), which was mentioned above, was solved by branch and bound framework (Androulakis (2000)). In that work, an important species in the considered detailed mechanism was defined as follows: if species j^{th} is removed from the detailed mechanism ($\langle \lambda_j \rangle_i = 0$) while all the others are kept, a reduced mechanism with an error θ' is found. If $\theta' \geq \epsilon$ that species is critical and cannot eliminate from the detailed mechanism. On the contrary, the species can be removed from the detailed mechanism and the search will be continued within the remaining $N' = N_s - 1$ species. The branch and bound search gives a global optimization solution. However, it requires a lot of time to run and hard to apply on large mechanism.

In this work, Genetic Algorithm (GA) has been applied as a searching procedure for mechanism reduction as in the work of Banerjee *et al.* (2006). The GA (Goldberg (1989)) presents a class of search and optimization tool by adapting the natural law of selection into a wide range of optimization problem. When GA is applied, the binary variable λ_j standing for species in a reduced mechanism is encoded to form a chromosome. Meanwhile, the total number of binary variables (λ_j) in a chromosome is number of species N_s in the concerned detailed mechanism. Starting with an initial

population, a set of particular chromosomes, GA evaluates the population and searches for the best solution to the optimal problem in the population. The next generation with the same number of chromosomes is generated from the previous ones, and the search is continued until the terminal condition is approached. Normally, GA search will stop after a predetermined number of generations or function evaluations.

The GA explores solution space by applying two slackly naturally genetic operators. They are crossover and mutation. The crossover exchange randomly substring of two selected genes from the considering population to form chromosomes in the next generations. It may be randomly one-point crossover or multiple-point crossover. For example, gene g1 and gene g2 with the length of 12 are randomly picked from a population:

$$g1 = 1\ 0\ 1\ 0\ 1\ 1\ 0\ |\ 0\ 1\ 1\ 1\ 0\ 0\ 0\ 0$$

$$g2 = 1\ 1\ 1\ 0\ 0\ 1\ 1\ |\ 0\ 1\ 0\ 0\ 1\ 0\ 1\ 1$$

the one-point crossover operator aimlessly points at a position in a string of gene as 7 in (signed by symbol “|” above). Then these genes exchange their substring forming new two gene g1' and g2' in the next generation:

$$g1' = 1\ 0\ 1\ 0\ 1\ 1\ 0\ 0\ 1\ 0\ 0\ 1\ 0\ 1\ 1$$

$$g2' = 1\ 1\ 1\ 0\ 0\ 1\ 1\ 0\ 1\ 1\ 1\ 0\ 0\ 0\ 0$$

To avoid bouncing a local optimum, GA applies mutation operator as a second searching agent. This operator arbitrarily takes a position in a gene then shifts the value of that position to the opposite value. For instance, the mutation picks points 4 in gene g3 = 1 0 1 0 1 0 0 1 1 0 1 0 1 1 0 to mutate. The gene g3' would be 1 0 1 1 1 0 0 1 1 0 1 0 1

1 0. Natural, the probability of mutation is very low. Therefore, GA mainly applies crossover.

Because GA cannot handle a nonlinear constrain of the optimal problem as defined in equation 5, an external consequence function is needed to penalty the impossible solutions while solving the unconstrained optimal problem (Michalewicz et.al (1996)). Consequently, the optimal problem 4 can be reformed as:

$$\mathfrak{J} = \min_{\lambda \in g^N} \sum_{i=1}^{N_s} \lambda_i + \varpi \times \max(\chi - \delta, 0) \quad (12)$$

where the term $\varpi \times \max(\chi - \delta, 0)$ is external penalty. It equals to 0 when the constraint is not desecrated and takes a large positive value otherwise. Each reduced mechanism in a solution space is integrated by DVODE (Hindmarsh et.al (1983)), while the thermodynamic properties as well as the rate expressions are evaluated using CHEMKIN III package (Kee et.al (1996)). The number of generations for GA search is 400 with 20 populations each

2.3. Two-step reduction procedure

Although mathematical programming method can find a good reduced mechanism from any detailed mechanism, it requires a lot of time to implement. For example, it took nearly 8 seconds to integrate 1 function of GRI-3.0 mechanism with 53 species and 325 reactions (Banerjee *et al.* (2006)) on Sun Solaris-8. So that, the CPU time for evaluating 5000 functions of GRI-3.0 requires more than 11 hours. Therefore, it is

uneconomic to apply mathematical programming into complicated mechanism having hundred of species and thousand of reactions such as pentane oxidation mechanism. On the other hand, the element accumulation flux cannot overuse to find a reduced mechanism. Because the accumulation of element flux of a species can show the “*relative role*” of that species in a mechanism. Some species, which have low element flux accumulation, might not be important and then can be further removed from the “skeleton” reduced mechanism. A high cut-off value can create a reduced mechanism involving these species, while a lower cut-off value can remove some critical species causing the profile deformation of some factors or generating a huge error as shown in figure 2 and figure 3. To save time, the flux analysis is applied first with a suitable cut-off value to trim some unimportant species from a complex detailed mechanism in order to condense the search space for the mathematical nonlinear programming.

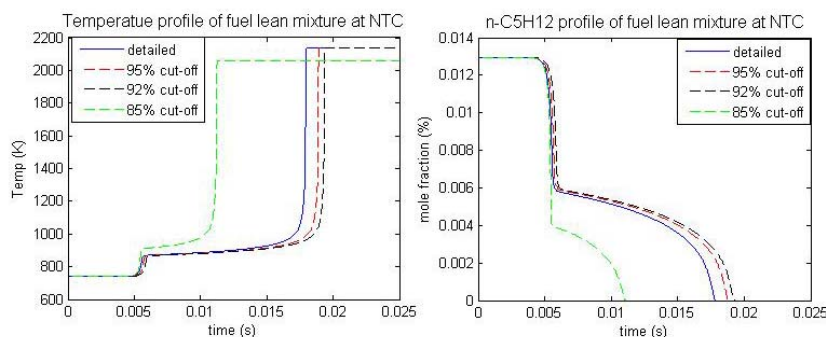


Figure 2: Temperature profile and n-C5H12 profile of the detailed mechanism, and the flux-reduced mechanisms with different cut-off values of fuel lean mixture at 740 K. (The detailed mechanism has 385 species and 1895 reactions. The flux-reduced mechanism with 85% cut-off contains 67 species and 240 reactions, the one with 92% cut-off has 113 species and 527 reactions, and the last with 95% cut-off has 124 species and 634 reactions).

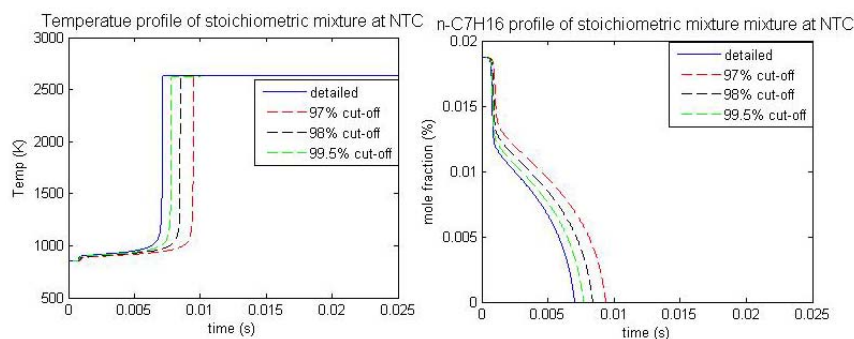


Figure 3: Temperature profile and n-C7H16 profile of the detailed mechanism, and the flux-reduced mechanism with different cut-off values of stoichiometric mixture at 850 K. (The detailed mechanism has 561 species and 2539 reactions. The flux-reduced mechanism with 97% cut-off contains 174 species and 895 reactions, the one with 98% cut-off has 191 species and 950 reactions, and the last with 99.5 % cut-off has 255 species and 1210 reactions).

2.4. Parallel Implementation

Although GA is an efficient search method, it can possibly take much time to find a good solution to some complicated problem such as finding a reduced mechanism for n-C₅H₁₂ and n-C₇H₁₆. We adapt the idea of master–worker parallel GA search in a report written by Erick Cantu’-Paz (1998) to solve a large problem. A parallel system is a group of n processors, which have their own unique rank from 0 to n-1, where the one with rank 0 is the master and the rests are workers. Communication between the master and its workers is managed by message passing interface library (MPI), a tool for parallel solving huge problems. The procedure of parallel GA is depicted in the following way. First, the master creates an initial population. And then, it sends chromosomes to the workers to calculate objective functions, which is the error of the reduced mechanisms encoded in the genes. These values are sent back to the master to evaluate the best solution, which has the smallest error, and a new population is generated. The process is repetitive if the termination condition fails. A small mechanism, which was created from GRI-3.0 by removing all nitrogen species, named grinoN containing 36 species and 219 reactions was used as a test case. The parallel GA implementation searched 50 generations with 50-population size. Figure 2 shows the acceleration of parallel GA calculation when the number of processors increases form 1 processors up to 18 processors. Since then number of processors increases, the calculation time decreases. The linear relationship between CPU time and number of processors shows that the more processors are used the faster calculation is.

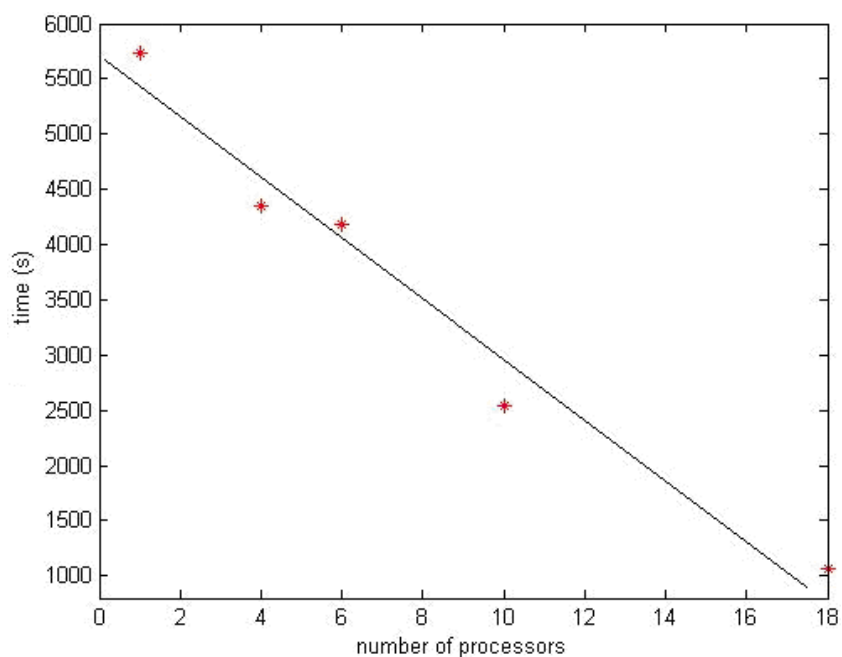


Figure 4: Calculation time vs. number processors for 2500 calculation of grinoN mechanism

2.5. Summary

A new mechanism reduction method for complicated mechanism is presented. In the two-stage mechanism reduction method, the flux analysis is used first to obtain a “skeleton” reduced mechanism from the detailed mechanism by eliminating the species, which has small element flux transferring. Because the removal species occupy a small amount of element flux, the obtaining reduced mechanism has a very small error to compare to that of the detailed mechanism. This reduced mechanism is, then, considered as a detailed mechanism for mathematical programming. The obtaining reduced mechanisms are solution of optimization problem, which is to find a subset of species from detailed mechanism while retaining a desired error. This optimization problem is

solved by GA, a stochastic optimal tool. Although, the flux analysis helps condensing the solution searching space, it requires a lot of time for GA to find a good reduced mechanism for a convoluted mechanism such as n-pentane combustion or n-heptane combustion. A parallel GA is used to speed up the calculation.

Chapter III

CASE STUDIES

3.1. Flux Reduction of Pentane Oxidation and Heptane oxidation

Flux analysis is a very powerful tool for mechanism reduction. The purpose of the first reduction step is to reduce the size of detailed mechanism while still retaining an acceptable accuracy for the GA reduction. Therefore, it is important to set a suitable threshold of accumulated element flux cut-off value for flux reduction. It should be noted that the first step (flux-based) reduction is critical in order to render the optimization-based reduction computationally tractable. The flux-based reduction identified correctly the required set of reactions/species needed to capture the complex auto-ignition characteristics of hydrocarbons. An unsuitable cut-off value can lose the aim of the first-step reduction of flux analysis approach. Since a reduced mechanism introduces some error, we can use the error to set a suitable threshold for flux reduction. At NTC oxidation, the temperature profile of n-C₅H₁₂ and n-C₇H₁₆ contains two ignition steps, at which there is a large jump. We define the first and the second ignition time (tig1 and tig2) as those at which the 1st derivative of temperature reaches its 1st and 2nd peaks as shown in figure 5. A reduced mechanism, which generates an acceptable average error of the first ignition time and second ignition time to compare to those of detailed mechanism, can be considered as a suitable flux-reduced mechanism. And the given cut-off threshold of that reduced mechanism can be used for other flux-reduction at low temperature and high temperature. Since 95% cut-off value for n-C₅H₁₂ and 99.5% for

n-C7H16 gave the average error of the first and the second ignition time is smaller than 10% in all the considered oxidation conditions. These values were selected as cut-off threshold for flux reduction step.

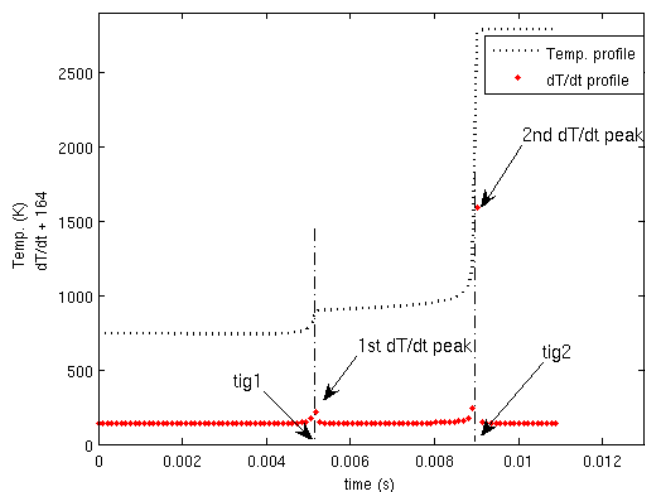


Figure 5: Defining 1st ignition time and 2nd ignition time based on temperature derivative.

The flux-analysis methodology was applied here for the reduction and characterization of pentane oxidation. The original detailed mechanism of pentane oxidation (385 species and 1895 reactions) based on a modified version of an n-heptane mechanism (Curran *et al.*(1998a)) was reduced by means of the flux analysis approach and a skeletal mechanism, (for example 126 species, 684 reactions in stoichiometric NTC oxidation), was identified by setting the cut-of value of 95%. This mechanism was subsequently reduced using the optimization approach to identify the final reduced representation. Nine oxidation conditions of n-C5H12 – air mixture diluted in Ar were examined. The low temperature oxidation simulations were at 600 K, the NTC ones were 740 K, and the high temperature oxidation simulations were 1000 K for fuel lean mixture (with equivalence ratio is 0.5), stoichiometric mixture (equivalence ratio is 1.0), and fuel

rich mixture (equivalence ratio is 2.0). As shown in table 2 with 95% cut-off, we can remove over 66% number of species and 61.69% number of reactions at low temperature oxidation and NTC oxidation for all cases. The number of species and reactions removed from the detailed mechanism is much larger at high temperature oxidation. The size of flux-reduced mechanisms and GA reduced mechanisms at high temperature oxidation are the smallest ones in all fuel lean, fuel rich, and stoichiometric mixture. It is easy to realize that the size of flux-reduced mechanisms and that of GA reduced mechanisms are quite similar in all composition cases. Furthermore, the reduced mechanisms of fuel rich mixture are always the largest ones.

Similar to n-pentane reduction, the detailed mechanism of n-heptane oxidation mechanism containing 561 species and 2539 reactions was first reduced by applying flux analysis approach with the cut-off value is 99.5 % to obtain a skeleton mechanism for an arbitrary condition (for instance, 203 species and 1063 reaction in fuel rich high temperature oxidation). This skeleton mechanism was then supplied to GA reduction as detailed mechanism. Nine oxidation conditions of n-heptane – air mixture, were considered with the charge density is 138.5 mol/m^3 . The low temperature oxidation experiments were carried at 550 K, the NTC ones were at 850 K, and high temperature oxidation simulations were at 1000 K for fuel lean mixture (equivalence ratio is 0.5), stoichiometric mixture (equivalence ratio is 1.0), and fuel rich mixture (equivalence ratio is 2.0). As can be seen in table 1, the first reduction step removed over 50% number of species and reactions in every case. Furthermore, the size of flux-reduced mechanisms does not change much from fuel lean to fuel rich. However, the size of GA reduced mechanisms is quite different from low temperature to high temperature oxidation. The

smallest ones are the reduced mechanisms at high temperature oxidation reduced mechanisms while the size of reduced mechanisms at low temperature oxidation is a little smaller than the ones at NTC. The second reduction helps to remove over more 30% number of species and nearly more 50% number of reactions.

| Condition | | n-pentane | | | | n-heptane | | | |
|--|--------|-------------------------------|----------------|-------------------------------|----------------|-------------------------------|----------------|-------------------------------|----------------|
| | | 1 st reduced mech. | | 2 nd reduced mech. | | 1 st reduced mech. | | 2 nd reduced mech. | |
| | | N _s | N _r | N _s | N _r | N _s | N _r | N _s | N _r |
| Fuel lean mixture ($\phi = 0.5$) | High T | 89 | 492 | 44 | 170 | 199 | 1021 | 120 | 506 |
| | NTC | 124 | 629 | 94 | 357 | 260 | 1215 | 160 | 731 |
| | Low T | 129 | 634 | 113 | 393 | 271 | 1193 | 178 | 657 |
| Stoichiometric mixture ($\phi = 1.0$) | High T | 83 | 485 | 40 | 135 | 195 | 1024 | 103 | 477 |
| | NTC | 126 | 684 | 83 | 372 | 255 | 1210 | 176 | 790 |
| | Low T | 124 | 673 | 103 | 387 | 278 | 1338 | 171 | 585 |
| Fuel rich mixture ($\phi = 2.0$) | High T | 93 | 557 | 44 | 199 | 203 | 1063 | 114 | 591 |
| | NTC | 129 | 726 | 98 | 473 | 258 | 1244 | 175 | 705 |
| | Low T | 122 | 714 | 98 | 439 | 275 | 1406 | 162 | 632 |

Table 1: The size of the flux-reduced mechanisms and the GA-reduced mechanisms of n-pentane and n-heptane oxidation (N_s is number of species; N_r is number of reactions)

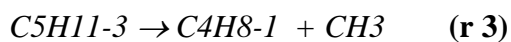
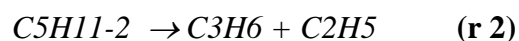
3.2. GA Reduction of n-pentane and n-heptane Oxidation

- **High temperature oxidation of n-C₅H₁₂**

High temperature oxidation of hydrocarbon responds to the formation of NO_x compounds and is also one of the key factors for ignition in spark-ignition (SI) engine and compress-ignition (CI) engine. Understanding the high temperature oxidation of fuel is important for combustion engine design and environment. The reduction of n-C₅H₁₂ – air mixture diluted in Ar at high temperature oxidation were carried out at 1000 K for fuel rich mixture ($\phi = 2.0$), stoichiometric ($\phi = 1.0$), and fuel lean ($\phi = 0.5$). Figure 6 presents the profile of temperature and some species of detailed mechanism, flux-reduced mechanisms, and GA reduced mechanisms as well as main reaction pathways at high temperature oxidation of n-C₅H₁₂. As can be seen on the left hand sides of figure 6a, 6b, and 6c, the profiles coming from the GA reduced mechanisms are quite closed to those of the flux-reduced mechanisms. With 95% cut-off, the flux-reduced mechanisms can predict the behavior of the mixture with acceptable accuracy. The GA reduced mechanisms can do very well. It should be noted that the GA reduction eliminated over 50% of species and 70% of reaction from flux-reduced mechanism. It is really a great reduction.

The reaction pathways mainly occur at high temperature oxidation via β - scission of alkyl radicals producing smaller olefin compounds, and then further decompose to other species with the presence of very active radical such as hydroxyl ($\dot{O}H$) and oxygen (\dot{O}) (Curran *et al.* (2002)) after hydrogen abstraction reaction from fuel. The main reaction

pathways from n-C₅H₁₂ of detailed mechanism, the flux-reduce mechanisms and the GA reduced mechanisms of fuel rich, stoichiometric, and fuel lean mixture are presented on the right hand sides of figure 6a, 6b, and 6c. As shown in the flux diagrams, the dotted lines present the pathways eliminated by the flux-reduction or the GA reduction step, and the solid lines are the pathways in final reduced mechanism. The thicker of the lines is the larger of element flux transfers through those pathways. It is clear that the species eliminated by flux-reduction step - the left hand side path signed 1st reduction - are quite similar in all cases. By removing the β - scission products whose accumulated element flux is greater than the threshold, the flux reduction disabled the reaction channels starting from these species and reactions involving these species. Further more, while searching for optimum set of species, the GA reduction removed some more species, such as C₃H₄-P, C₃H₄-A, C₃H₈, etc. And then it eliminated the reactions involving these removal species. The main β - scission reactions from C₅H₁₁ radicals are following.



They all remain in the GA reduced mechanism of fuel rich at high temperature oxidation. However, the GA reduction removed n-C₃H₇ and other species, which are β - scission products of C₅H₁₁-1, such as C₅H₁₀-1 in fuel lean mechanism. Therefore, reaction (r 1) was disabled. It made way for isomerization reaction of C₅H₁₁-1 (r 4) to become stronger leading to enhance reaction pathway via (r 2).



Similar to the lean case, the GA reduction of stoichiometric mixture at high temperature oxidation omitted n-C₃H₇ and other β- scission products from C₅H₁₁-1 radical as well as C₄H₈-1 species. Therefore, reaction (r 1) and (r 3) were deactivated. Consequently, besides enhancing pathway from C₅H₁₁-2 radical through reactions (r 4) and (r 2) as mentioned previously, another β- scission reaction, (r 5), from C₅H₁₁-3 becomes dominant leading to an improvement of pathway from C₅H₁₀-2 species.



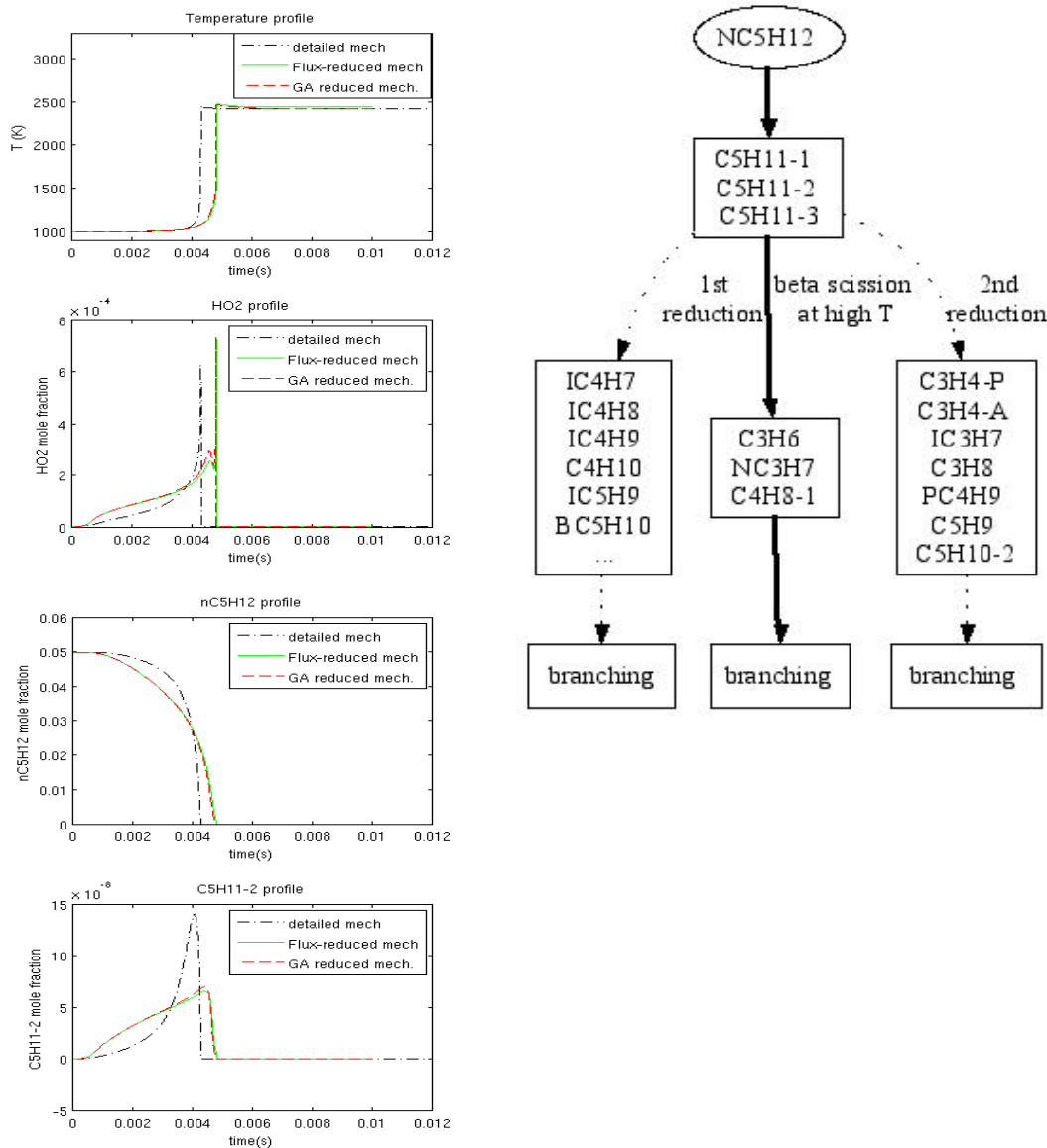


Figure 6.a: High temperature oxidation (1000 K) of fuel rich of n-C₅H₁₂ - air mixture (equivalence ratio = 2.0. The detailed mechanism has 385 species and 1895 reactions. The flux-reduced mechanism contains 93 species and 557 reactions. And the GA reduced mechanism consists of 44 species and 199 reactions. Temperature profile and species profiles are on the left. Reaction pathways are on the right.)

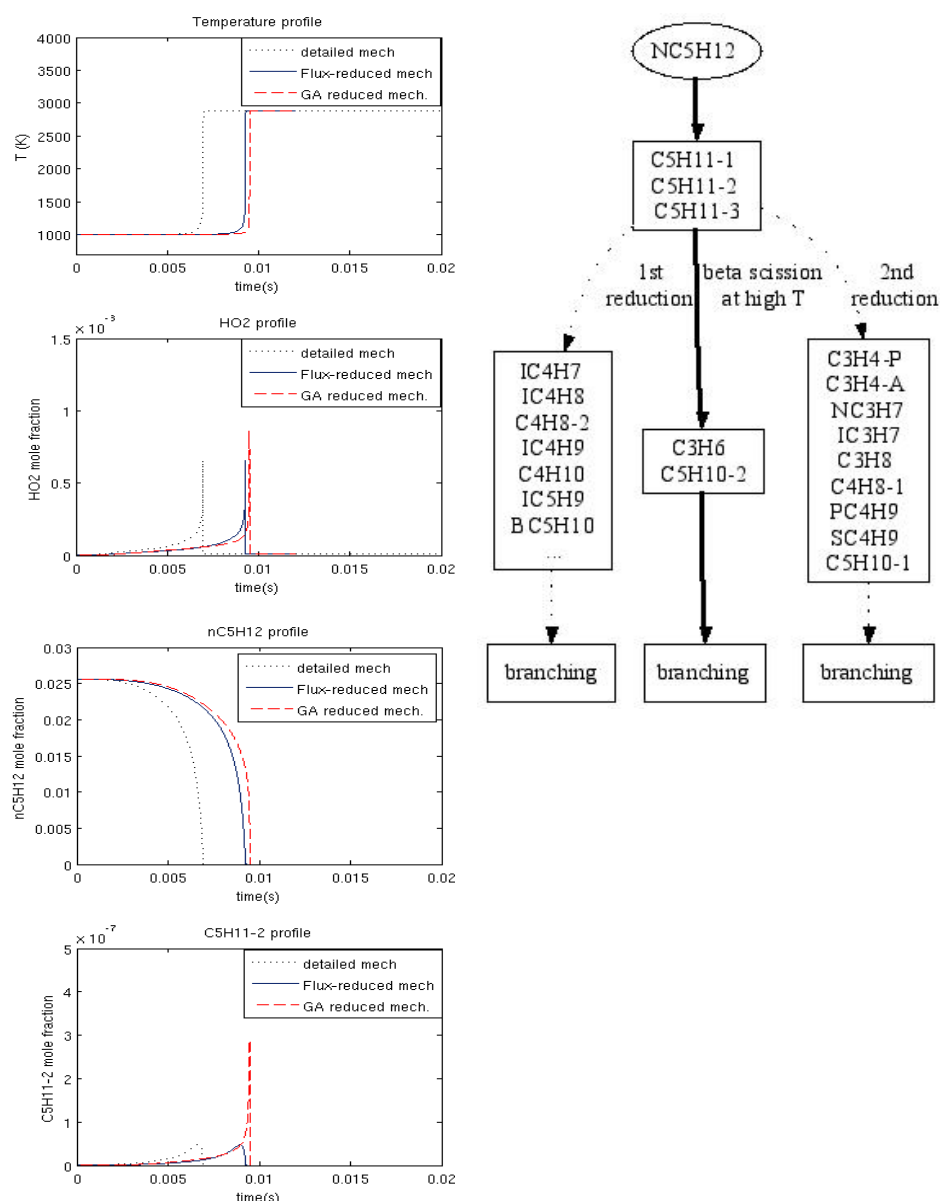


Figure 6.b: High temperature oxidation (1000 K) of stoichiometric of n-C₅H₁₂ – air mixture (equivalence ratio = 1.0. The detailed mechanism has 385 species and 1895 reactions. The flux-reduced mechanism contains 93 species and 557 reactions. And the GA reduced mechanism consists of 40 species and 135 reactions. Temperature profile and species profiles are on the left. Reaction pathways are on the right.)

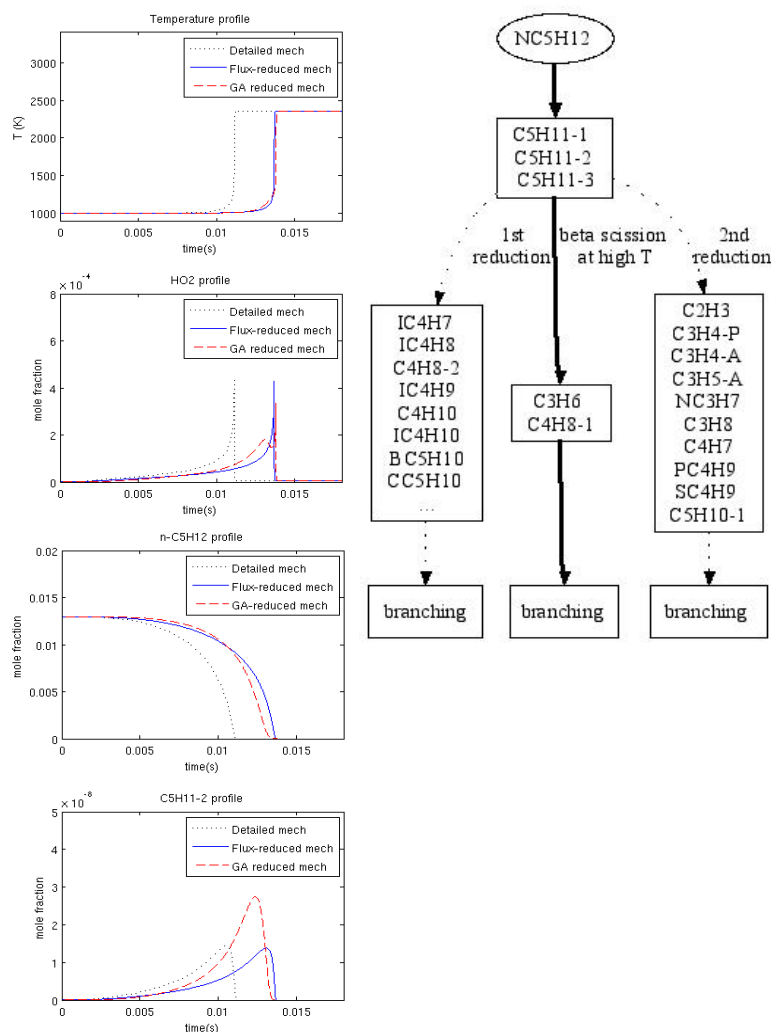
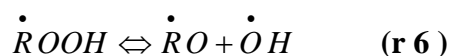


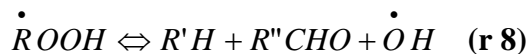
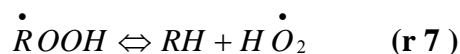
Figure 6.c: High temperature oxidation (1000 K) of fuel lean of n-C₅H₁₂ – air mixture (equivalence ratio =0.5. The detailed mechanism has 385 species and 1895 reactions. The flux-reduced mechanism contains 93 species and 557 reactions. The GA reduced mechanism consists of 44 species and 170 reactions. Temperature profile and species profiles are on the left. Reaction pathways are on the right.)

- **NTC temperature oxidation of n-C5H12**

At some range of temperature, the oxidation rate decreases when temperature increases for the fuel having long carbon chain. This phenomenon is known as *negative temperature coefficient* (NTC). The chemistry at NTC is very complicated because there are numerous oxidation channels. Temperature profile and species profiles as well as reaction pathways of the detailed mechanism, the flux-reduced mechanisms, and the GA reduced mechanisms at NTC of mixture ($\phi = 2.0$), stoichiometric ($\phi = 1.0$), and fuel lean ($\phi = 0.5$) are shown in figure 7 where the left hand sides are the profiles of temperature and species, the right hand sides are the reaction pathways diagrams. As can be seen on the left hand side of figure 7a, 7b, and 7c, the GA reduced mechanisms can predict very well the two stage-ignition of n-C5H12 although the GA reduction removed around 25% of species and 40% of reactions from flux-reduced mechanism. The temperature profile of fuel rich condition shows that the mixture governed by flux-reduced mechanism ignites a little bit sooner than the detailed mechanism does. It is possible that the 1st step reduction eliminated some species, which affect the formation of some active radicals such as hydroxyl ($\dot{O}H$); oxygen (\dot{O}) or HO_2^\bullet , leading to over prediction at NTC.

Simmie (2003) summarized from experiment of Minneti *et al.*, the NTC phenomena of hydrocarbon oxidation of n-C5H12 occurs in a range of temperature from 645 K to 890K, when the energy barrier of the dissociation reaction of RCOOH radicals becomes easy to overcome. It causes many propagation channels such as cyclic ethers, conjugate olefin compounds and HO_2^\bullet radical, and β -scission products as follows:





The HO_2^\bullet radical is quite stable. It is less active than $\dot{O}H$ radical. As a result, it reduces the activity of the system (Androulakis (2004), Curran *et al.*(1998b)).

In the reaction pathway diagrams, the thickness of the lines indicates the main reaction channels. The solid line are the pathways remaining in the GA reduced mechanisms, the dotted lines are the reaction pathways eliminated by the flux-reduction or the GA reduction. The species and pathways, which are assigned 1st reduction and connected by dotted lines on the left path of reaction pathway diagrams, were removed by flux because the accumulation element flux of these species is smaller than cut-off value (95%). As final reduction step, the GA reduction continued trimming the reaction pathways signed 2nd reduction from other species, for example C5H10OOH1-4 and C5H10OOH3-2 in fuel rich, or C5H10OOH2-5 in stoichiometric mixture, or C5H10OOH2-1 and C5H10OOH2-5 in fuel lean mixture.

We observe from figure 7 a striking phenomenon that is the pathways occurring in different conditions show up at the same time. They are namely the β - scission reactions from C5H11OOH radicals for NTC chemistry, β - scission reactions from C5H11 radicals for high temperature, and the reactions that lead to the formation of nC5KETO compounds for the low temperature oxidation of n-C5H12. More interestingly, the high temperature β - scission reactions from C5H11 radicals are dominant in fuel rich mixture while the pathways of low temperature slightly dominate in

fuel lean mixture. These phenomena show that fuel rich mixture tends to behave like high temperature oxidation chemistry and fuel lean mixture acts like low temperature oxidation chemistry even though the initial condition is NTC.

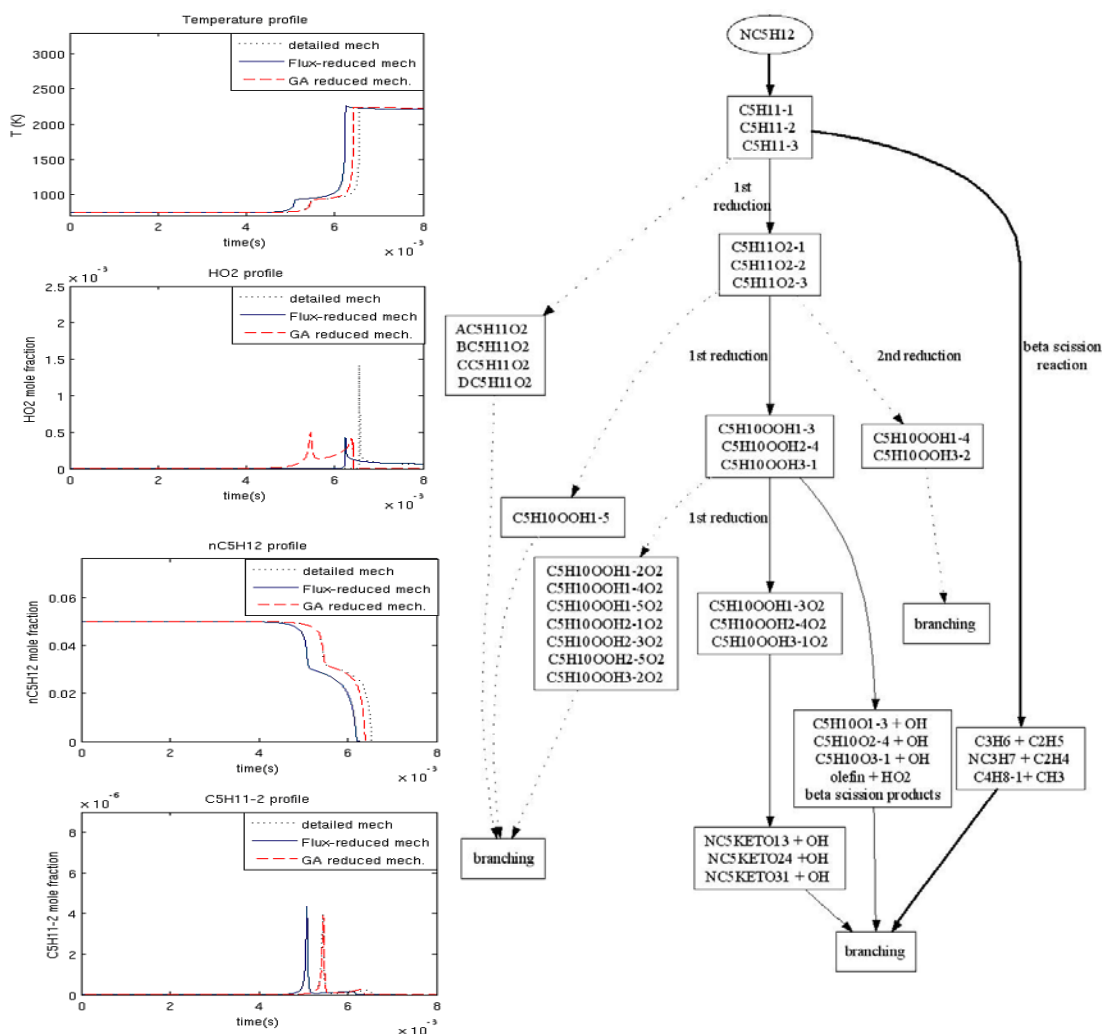


Figure 7.a: NTC temperature oxidation (740 K) of fuel rich of n-C₅H₁₂ - air mixture (equivalence ratio = 2.0. The detailed mechanism has 385 species and 1895 reactions. The flux-reduced mechanism contains 129 species and 726 reactions. The GA reduced mechanism consists of 98 species and 473 reactions. Temperature profile and species profiles are on the left. Reaction pathways are on the right.)

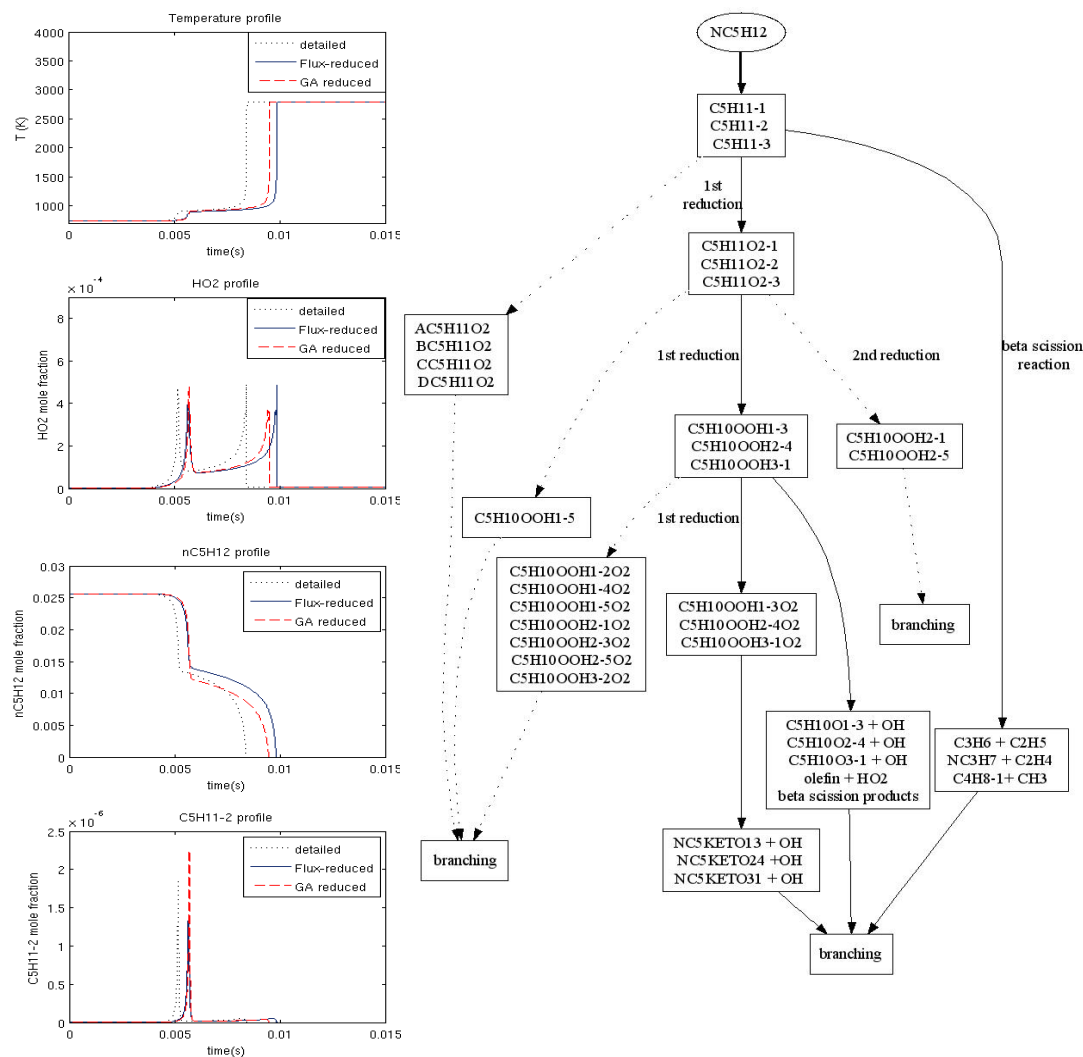


Figure 7.b: NTC temperature oxidation (740 K) of stoichiometric n-C5H12 – air mixture (equivalence ratio = 1.0. The detailed mechanism has 385 species and 1895 reactions. The flux-reduced mechanism contains 126 species and 684 reactions. The GA reduced mechanism consists of 83 species and 372 reactions. Temperature profile and species profiles are on the left. Reaction pathways are on the right.)

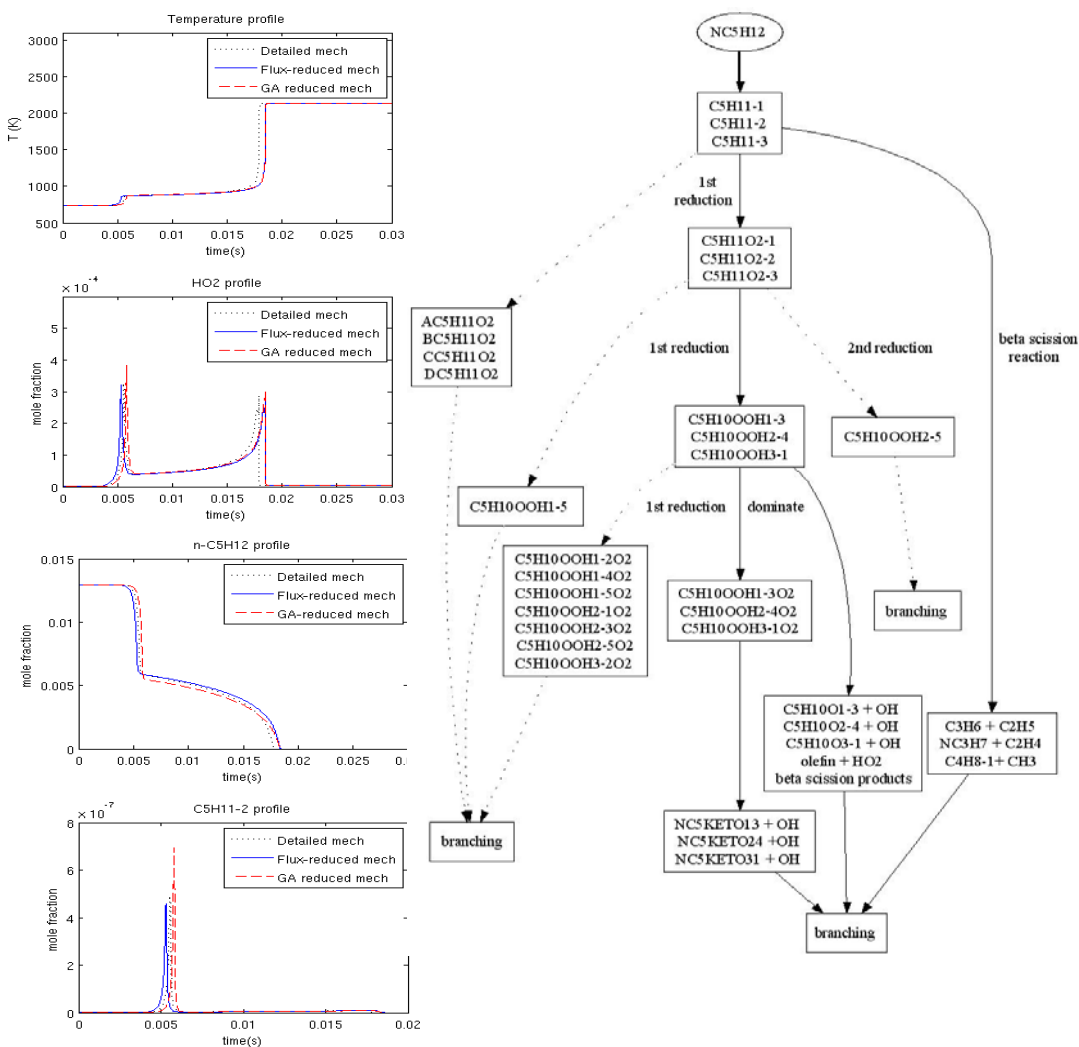


Figure 7.c: NTC temperature oxidation (740 K) of fuel lean of n-C5H12 –air mixture (equivalence ratio = 0.5. The detailed mechanism has 385 species and 1895 reactions. The flux-reduced mechanism contains 124 species and 629 reactions. The GA reduced mechanism consists of 94 species and 357 reactions. Temperature profile and species profiles are on the left. Reaction pathways are on the right.)

- **Low temperature oxidation of n-C₅H₁₂**

Low temperature autoignition is a phenomenon of critical technological importance. Induction times of hydrocarbon oxidation require complex chemistry involving thousands of species and reactions. The complexity of low temperature oxidation of n-C₅H₁₂ and n-C₇H₁₆ has been investigated in the RCM at Lille by Minetti *et al.* (1995). The reaction pathways occurring at low temperature oxidation are mainly the ones to form carbonylhydroperoxide species (Curran *et al.* (1998)). These species, then, decompose via two different pathways with lower energy to generate an aldehyde compound and two OH radicals or a radical and an OH radical as mentioned in (Androulakis (2004)).

The low temperature oxidation simulations of n-C₅H₁₂ – air mixture diluted in Ar were carried out at 600 K for fuel rich ($\phi=2.0$), stoichiometric ($\phi=1.0$), and fuel lean ($\phi=0.5$) mixture. Figure 8 presents the profiles of temperature and species as well as the reaction pathways of the detailed mechanism, the flux-reduced mechanisms, and the GA reduced mechanisms. As shown on the left hand side of figure 8a, 8b, and 8c, the GA reduced mechanisms predicted very well behavior of low temperature oxidation of n-C₅H₁₂. The profile of temperature and species of GA reduced mechanism are greatly similar to those of flux-reduced mechanism. Temperature profile and species profiles in figure 8c show that the Flux-reduced mechanism and GA reduced mechanism over predicted for fuel lean mixture.

The chain branching of low temperature oxidation of n-C₅H₁₂ of fuel rich, stoichiometric, and fuel lean mixture were displayed on the right hand side of figure 8a,

b, and c. The thickness of lines stands for the amount of carbon flux transporting through the pathways. The solid lines are the reaction pathways remaining in GA reduced mechanisms. Dotted lines are the ones eliminated by the flux reduction or the GA reduction. The species and reaction pathways decoupled by 1st step reduction were assigned 1st reduction and on the left part of reaction pathway diagrams. With 95% cut-off value, the flux-reduction trimmed the reaction pathways, whose accumulation flux of oxygen, hydrogen, and carbon is greater than cut-off value, and hence, indirectly removed the reactions involving these species. The remaining species were further analyzed by the GA reduction to figure out the removable pathways, which were labeled as 2nd reduction in pathways diagrams, such as the channel from C5H10OOH1-4, and C5H10OOH3-1O2 in figure 8a for fuel rich, or n-C5KETO14 in figure 8b for stoichiometric, and C5H10OOH2-3 in figure 8c for fuel lean mixture.

It is very amazing that the β - scission reactions, the ones stand for high temperature oxidation, from C5H11 radicals occur at low temperature oxidation of fuel rich mixture in figure 8a. Reaction pathways analysis showed that the amount of carbon flux transforming via this pathways is as equal as that of low temperature chemistry in fuel rich mixture oxidation. Furthermore, we also see the reaction leading to the formation of HO_2^* species from β - scission reactions of C5H10OOH radicals in figure 8b. It means that the NTC chemistry starts to occur at low temperature oxidation in stoichiometric mixture oxidation.

Figure 8.a: Low temperature oxidation (600 K) of fuel rich of n-C₅H₁₂ – air mixture (equivalence ratio = 2.0. The detailed mechanism has 385 species and 1895 reactions. The flux-reduced mechanism contains 122 species and 714 reactions. The GA reduced mechanism consists of 98 species and 439 reactions. Temperature profile and species profiles are on the left hand side. Reaction pathways are on the right.)

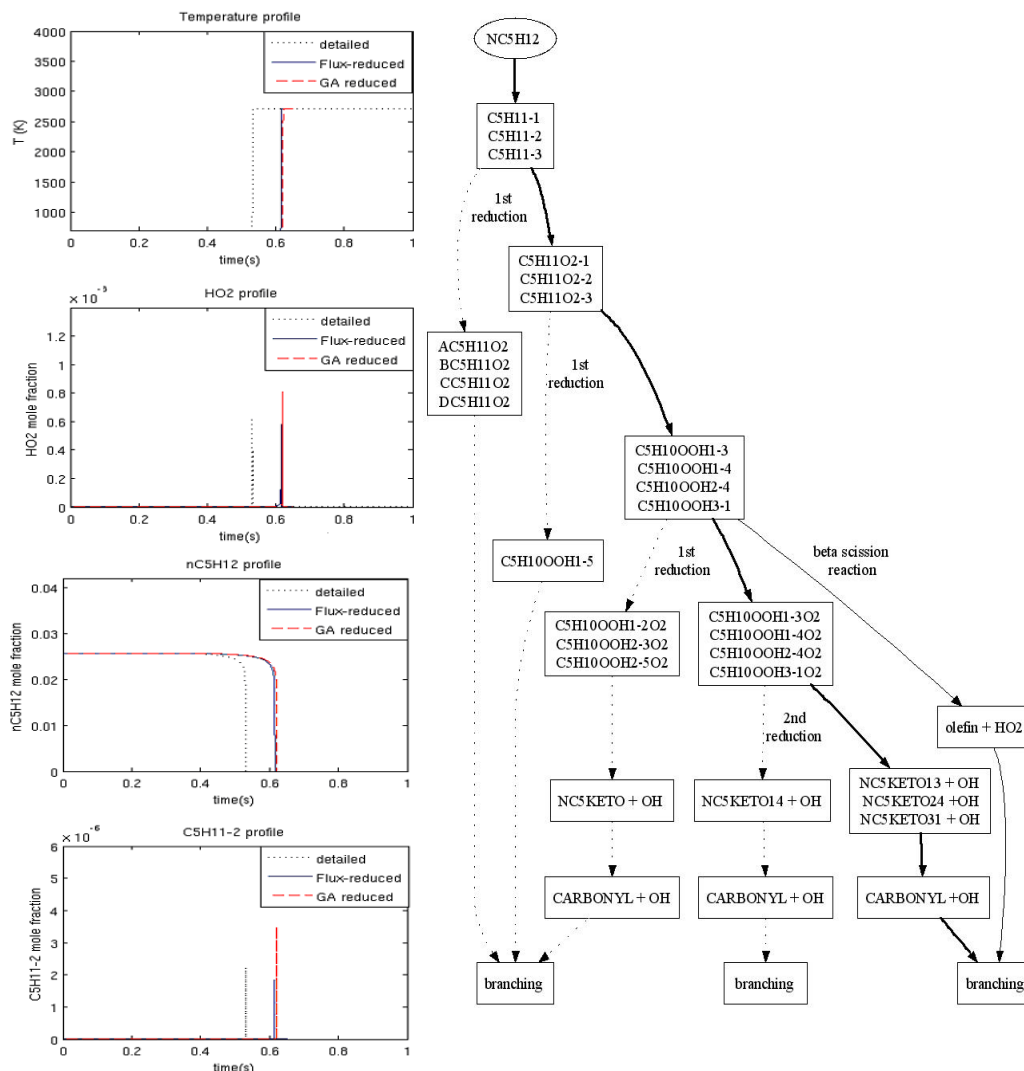


Figure 8.b: low temperature oxidation (600 K) of stoichiometric n-C₅H₁₂ – air mixture (equivalence ratio = 1.0. The detailed mechanism has 385 species and 1895 reactions. The flux-reduced mechanism contains 124 species and 673 reactions. The GA reduced mechanism consists of 103 species and 387 reactions. Temperature profile and species profiles are on the left hand side. Reaction pathways are on the right.)

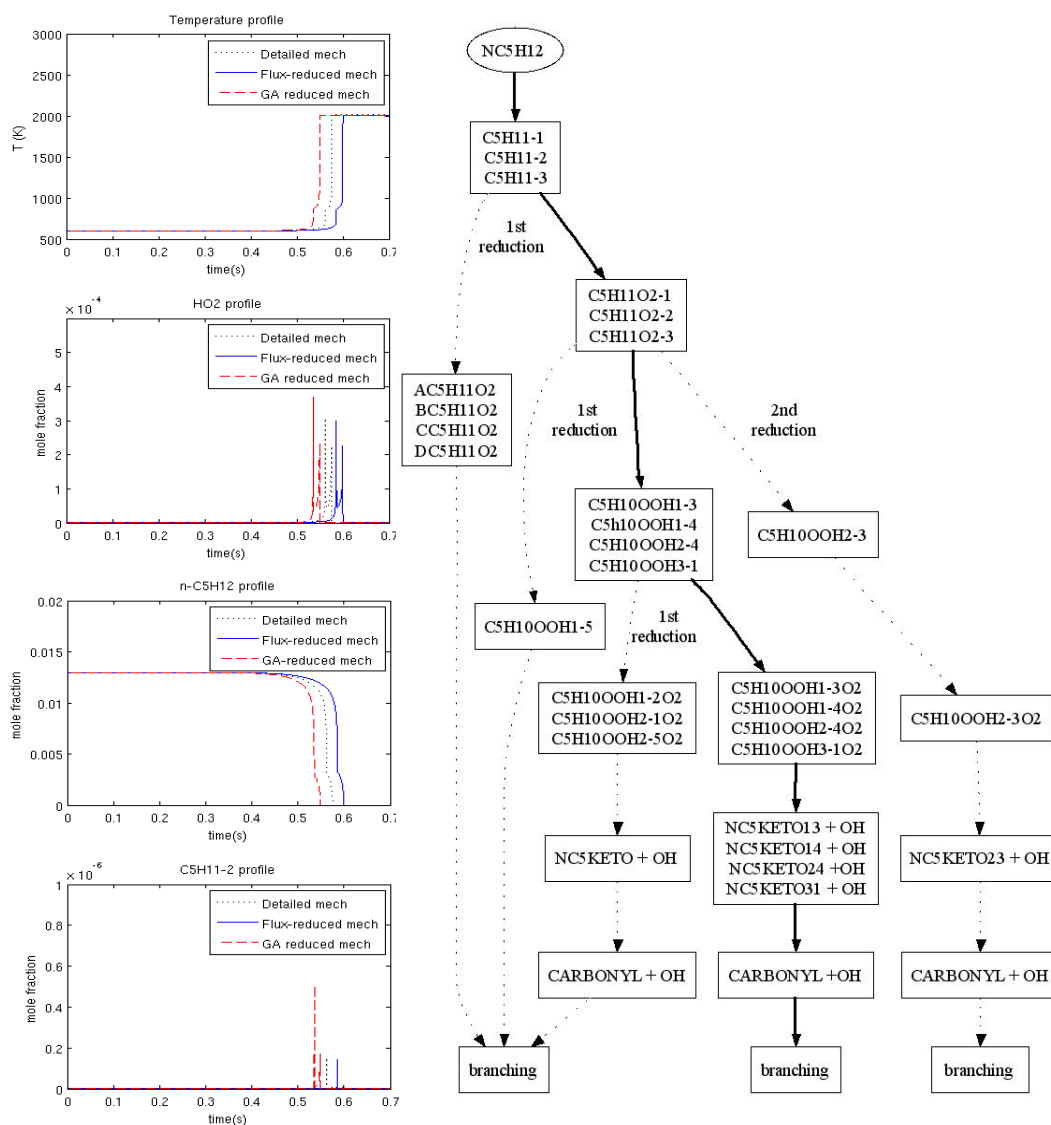
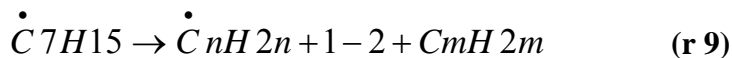


Figure 8.c: Low temperature oxidation (600 K) of fuel lean of n-C₅H₁₂ – air mixture (equivalence ratio = 0.5. The detailed mechanism has 385 species and 1895 reactions. The flux-reduced mechanism consists of 129 species and 634 reactions. The GA reduced mechanism contains 113 species and 393 reactions. Temperature profile and species profiles are on the left hand side. Reaction pathways are on the right.)

- **High temperature oxidation of n-heptane oxidation**

The reductions of n-heptane – air mixture at high temperature were carried out at 1000 K for fuel rich (equivalence ratio is 2.0), stoichiometric (equivalence ratio is 1.0) and fuel lean (equivalence ratio is 0.5) mixture. Figure 9 presents temperature and species profiles as well as reaction pathway diagram of the detailed mechanism, the flux-reduced mechanisms, and the GA reduced mechanisms. As can be seen on the left hand side of figure 9, the profiles of temperature and species coming from the flux-reduced mechanisms are very close to that of detailed mechanism. The temperature and species profiles of GA reduced mechanism shows that GA reduced mechanisms predicts very well the behavior of oxidation process although the GA reduction eliminated about 30% species and 50% reactions from the flux-reduced mechanism. The profile of temperature and species shows that the fuel rich mixture ignites very soon while stoichiometric mixture requires longer time and the fuel lean ignites latest.

It is believed that olefin and alkyl radicals formed by β - scission reaction (Curran *et al.* (1998a, 1998b), Curran *et al.* (2002)) occur mainly at high temperature oxidation as follow.



The reaction pathway diagrams on the right hand side of figure 9 reveal the high temperature oxidation chemistry of n-heptane – air mixture where the thickness of lines mentions the amount of carbon flux transporting through those pathways. The solid lines are the reaction pathways remaining in GA reduced mechanism. The dotted lines are the ones eliminated by the 1st reduction or the 2nd reduction. The reaction pathways

eliminated by flux analysis are on the left part of the diagrams. These pathways generate numerous products of n-C₇H₁₅ decomposition reaction such as alkane rings, iso-C₄H₁₀ and so on. Species and reaction pathways, assigned by 2nd reduction on the right part of the diagram, were trimmed by GA reduction.

The reaction pathway analysis shows that beside the β - scission products of C₇H₁₅ radical decomposition via reaction (r9), we also see oxygen addition products such as C₇H₁₅O₂-1, C₇H₁₄OOH1-3, and C₇H₁₄O1-3 compound in reaction pathway diagram of fuel lean in figure 9c or C₇H₁₅O-3 in that of stoichiometric mixture in figure 9b. Since the energy barrier of oxygen addition to C₇H₁₅ radical is zero, the redundancy of oxygen in fuel lean and stoichiometric mixture enhances these pathways. However, β - scission reaction pathways of C₇H₁₅ decomposition via reaction (r9) are still dominant,

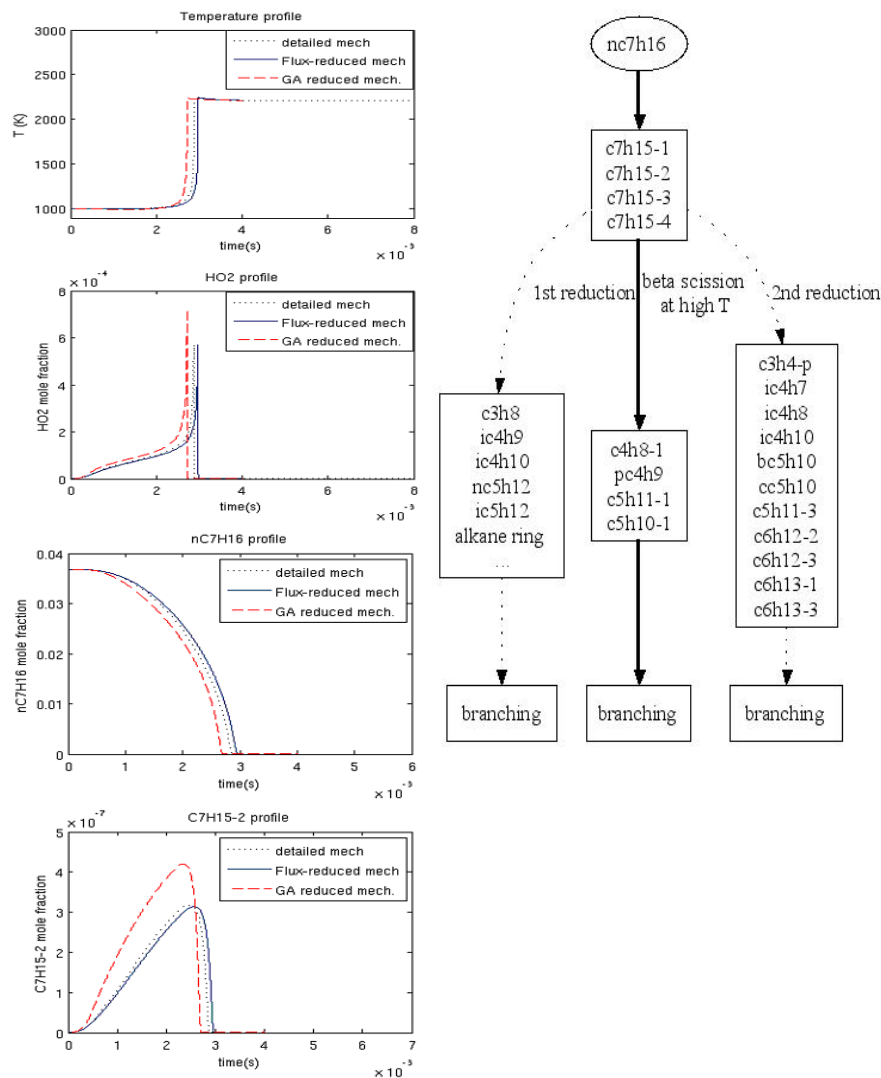


Figure 9.a: High temperature oxidation (1000 K) of fuel rich of n-C7H16 - air mixture (equivalence ratio = 2.0. The detailed mechanism has 561 species and 2539 reactions. The flux-reduced mechanism contains 203 species and 1063 reactions. And the GA reduced mechanism consists of 114 species and 591 reactions. Temperature profile and species profiles are on the left. Reaction pathway diagram is on the right.)

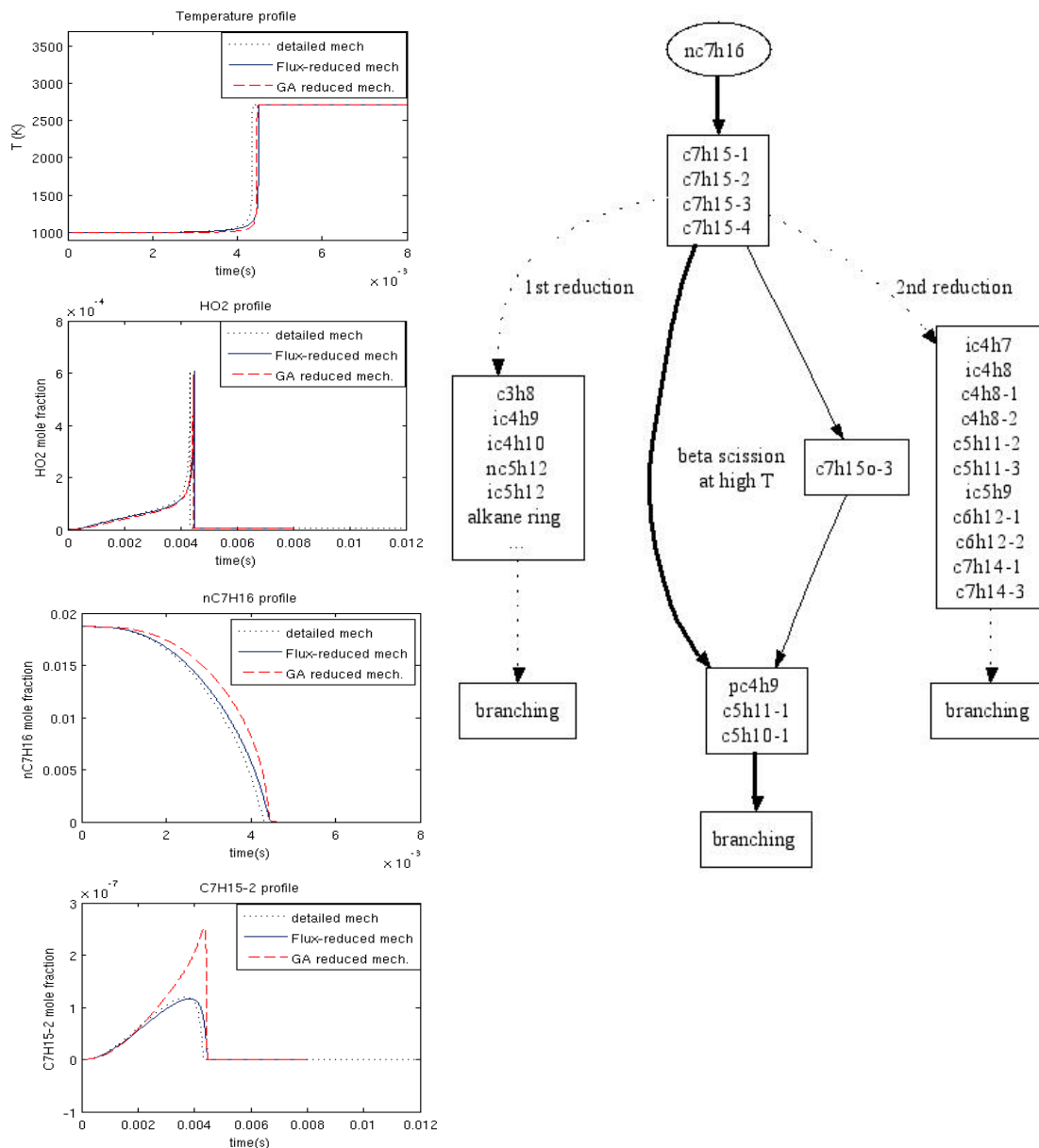


Figure 9.b: High temperature oxidation (1000 K) of stoichiometric n-C7H16 - air mixture (equivalence ratio = 1.0. The detailed mechanism has 561 species and 2539 reactions. The flux-reduced mechanism contains 195 species and 1024 reactions. The GA reduced mechanism consists of 103 species and 477 reactions. Temperature profile and species profiles are on the left. Reaction pathway diagram is on the right.)

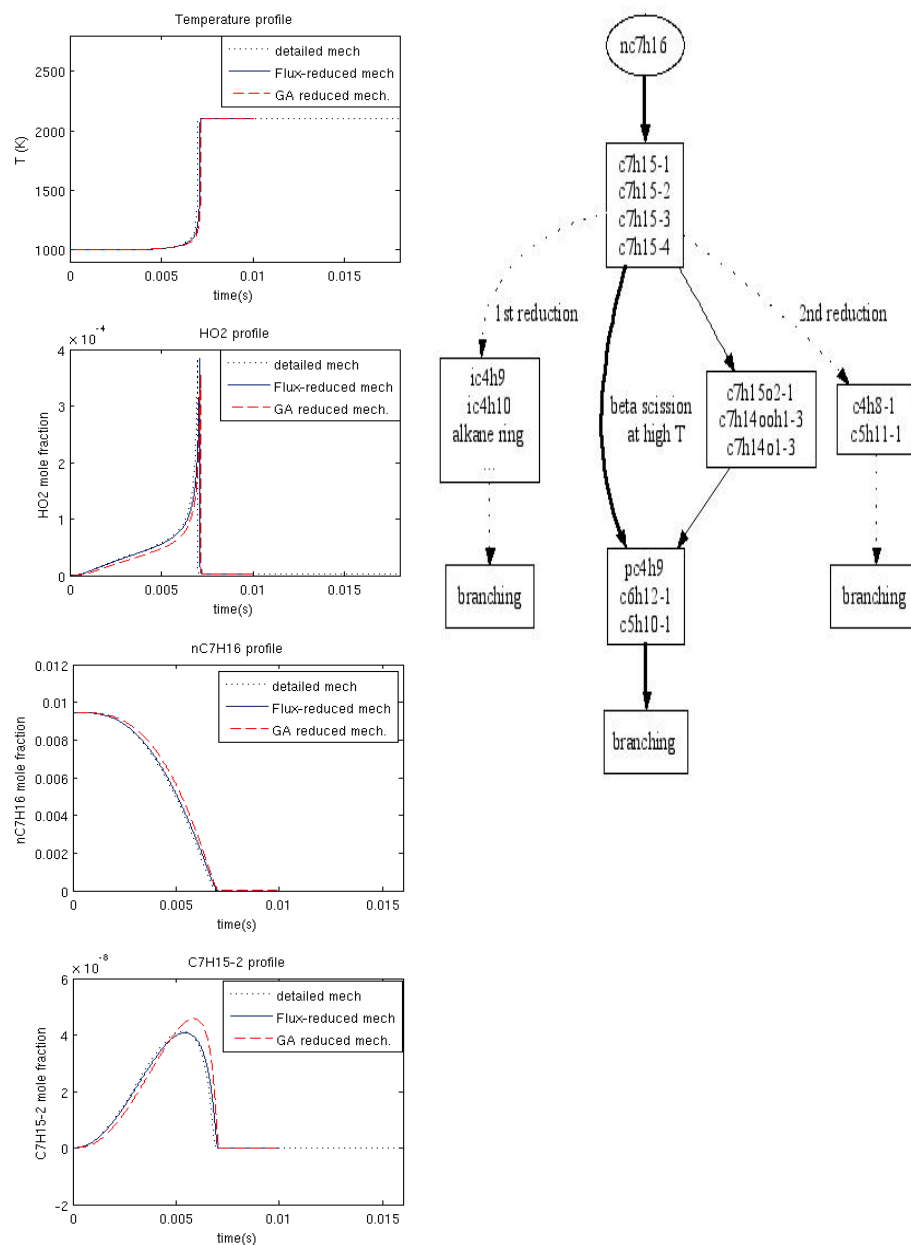


Figure 9.c: High temperature oxidation (1000 K) of fuel lean of n-C₇H₁₆ – air mixture (equivalence ratio = 0.5. The detailed mechanism has 561 species and 2539 reactions. The flux-reduced mechanism contains 199 species and 1021 reactions. The GA reduced mechanism consists of 120 species and 506 reactions. Temperature profile and species profiles are on the left. Reaction pathway diagram is on the right.)

- **NTC temperature oxidation of n-heptane oxidation**

The eliminations of n-heptane – air mixture at NTC were operated at 850 K for fuel rich, stoichiometric, and fuel lean mixture. Temperature and species profiles as well as reaction pathways diagram of detailed mechanism, flux-reduced mechanism, and GA reduced mechanism are presented in figure 10. As shown on the left hand sides of figure 10, there is great agreement between the flux-reduced mechanism and the detailed mechanism in all considered oxidation conditions. The GA reduction eliminated over 25% species in fuel rich and stoichiometric mixture and 30% species in fuel lean mixture. It indirectly disabled 45% reactions in fuel rich, 35% those in stoichiometric and 40% reactions from the flux-reduced mechanism, the GA reduced mechanisms can predict combustion of n-heptane – air mixture with very high accuracy. They all show the two-step ignition for every considered condition. Temperature and species profiles of fuel rich mixture approach plateau very soon, while it takes a little more time for that of stoichiometric and fuel lean mixture.

Reaction pathway diagrams, shown on the right hand sides of figure 10, reveal the complex chemistry channels of n-heptane oxidation at NTC. The solid lines are the pathways remaining in the final reduced mechanisms. The dotted lines, assigned by 1st reduction or 2nd reduction, are the reaction channels eliminated by the flux reduction or the GA reduction respectively. The thickness of the lines indicates the amount of carbon flux transferring through these reaction pathways. On the left part of reaction pathway diagrams in figure 10, the channels assigned with 1st reduction were eliminated by the flux analysis when the accumulated element flux of the species involving in these

channels is greater than cut-off threshold. The remaining of diagrams, involving both the solid lines and the dotted lines assigned with 2nd reduction, is flux-reduced mechanism, which is further reduced by GA.

At intermediate temperature, the alkyl radical decomposition reaction of C₇H₁₅ compounds becomes less important. Instead, oxygen addition reaction to these species is dominant leading to the formation of C₇H₁₅O₂ compounds and the activation of several complicated reaction channels. As mentioned in the NTC oxidation of n-C₅H₁₂, reactions (r 6), (r 7), and (r 8) characterize the NTC chemistry of n-heptane oxidation since the energy barrier of the dissociation reaction of RCOOH radicals becomes easy to overcome. Similarly to n-C₅H₁₂ oxidation of fuel rich mixture at NTC, we also see the β -scissor reactions, those mainly occur at high temperature oxidation, from C₇H₁₅ radicals in mechanism diagram of fuel rich mixture. However, these channels are not dominant as they are in the NTC oxidation of n-C₅H₁₂. Furthermore, the channels, which characterize the low temperature chemistry and lead to the formation of keto compounds, appear in the stoichiometric and fuel lean mixture oxidation. The reaction pathway analysis shows that the low temperature chemistry tends to be strong for fuel lean oxidation since the carbon flux transforming through these channels in fuel lean mixture is equal to the reaction pathways of NTC chemistry.

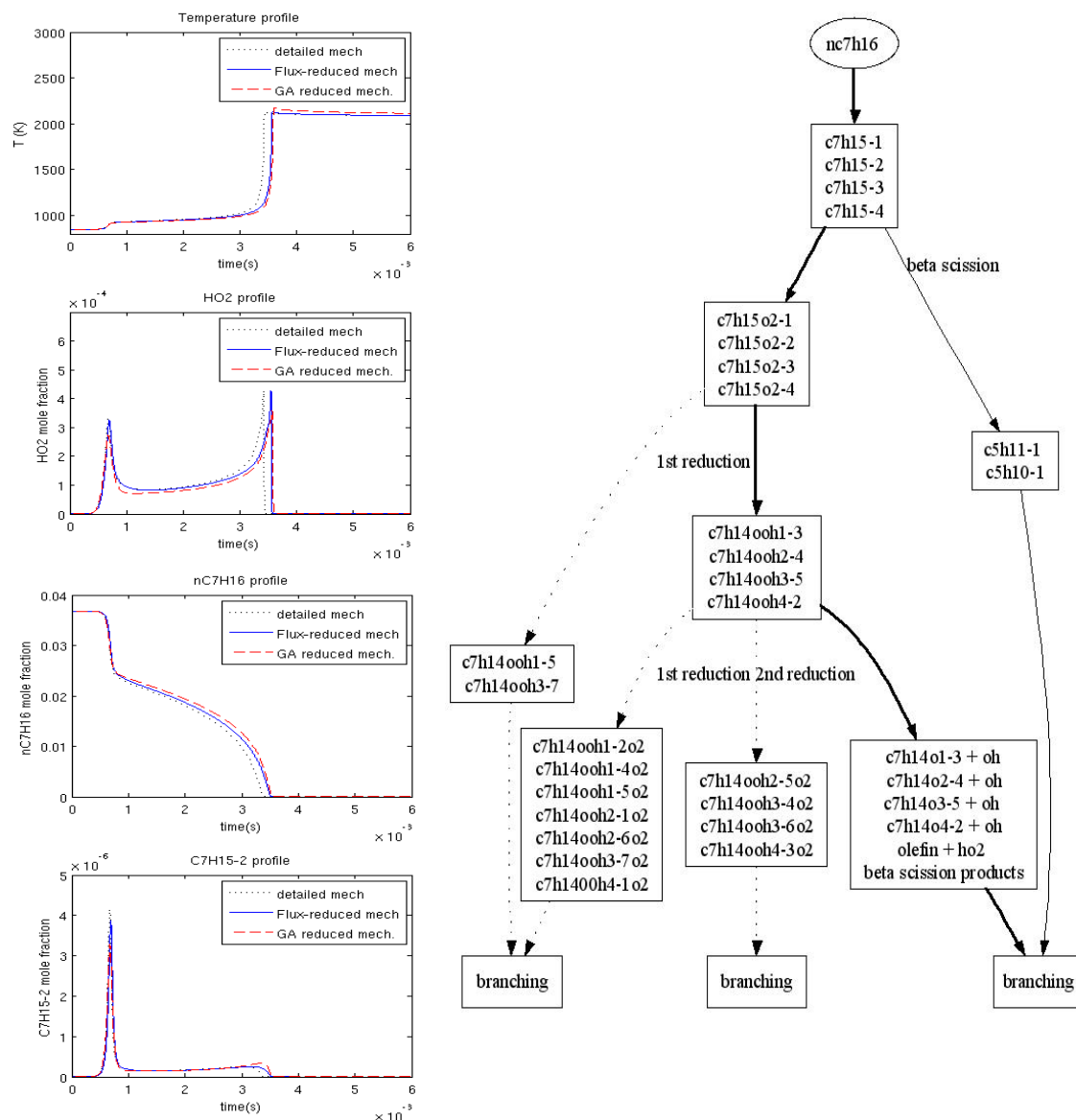


Figure 10.a: NTC temperature oxidation (850 K) of fuel rich of n-C₇H₁₆ - air mixture (equivalence ratio = 2.0. The detailed mechanism has 561 species and 2539 reactions. The flux-reduced mechanism contains 258 species and 1244 reactions. The GA reduced mechanism consists of 175 species and 705 reactions. Temperature profile and species profiles are on the left. Reaction pathway diagram is on the right.)

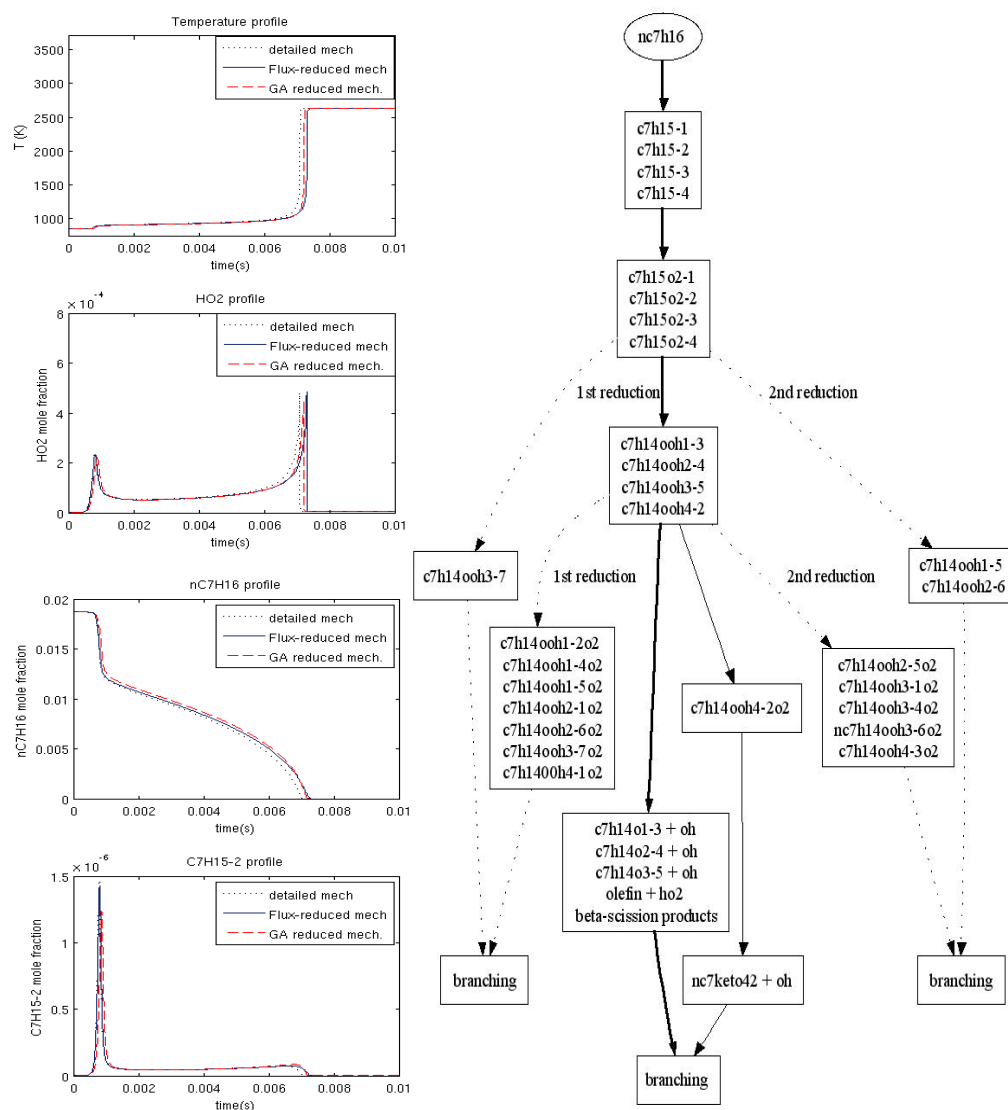


Figure 10.b: NTC temperature oxidation (850 K) of stoichiometric n-C7H16 – air mixture (equivalence ratio = 1.0. The detailed mechanism has 561 species and 2539 reactions. The flux-reduced mechanism contains 255 species and 1210 reactions. The GA reduced mechanism consists of 176 species and 790 reactions. Temperature profile and species profiles are on the left. Reaction pathway diagram is on the right)

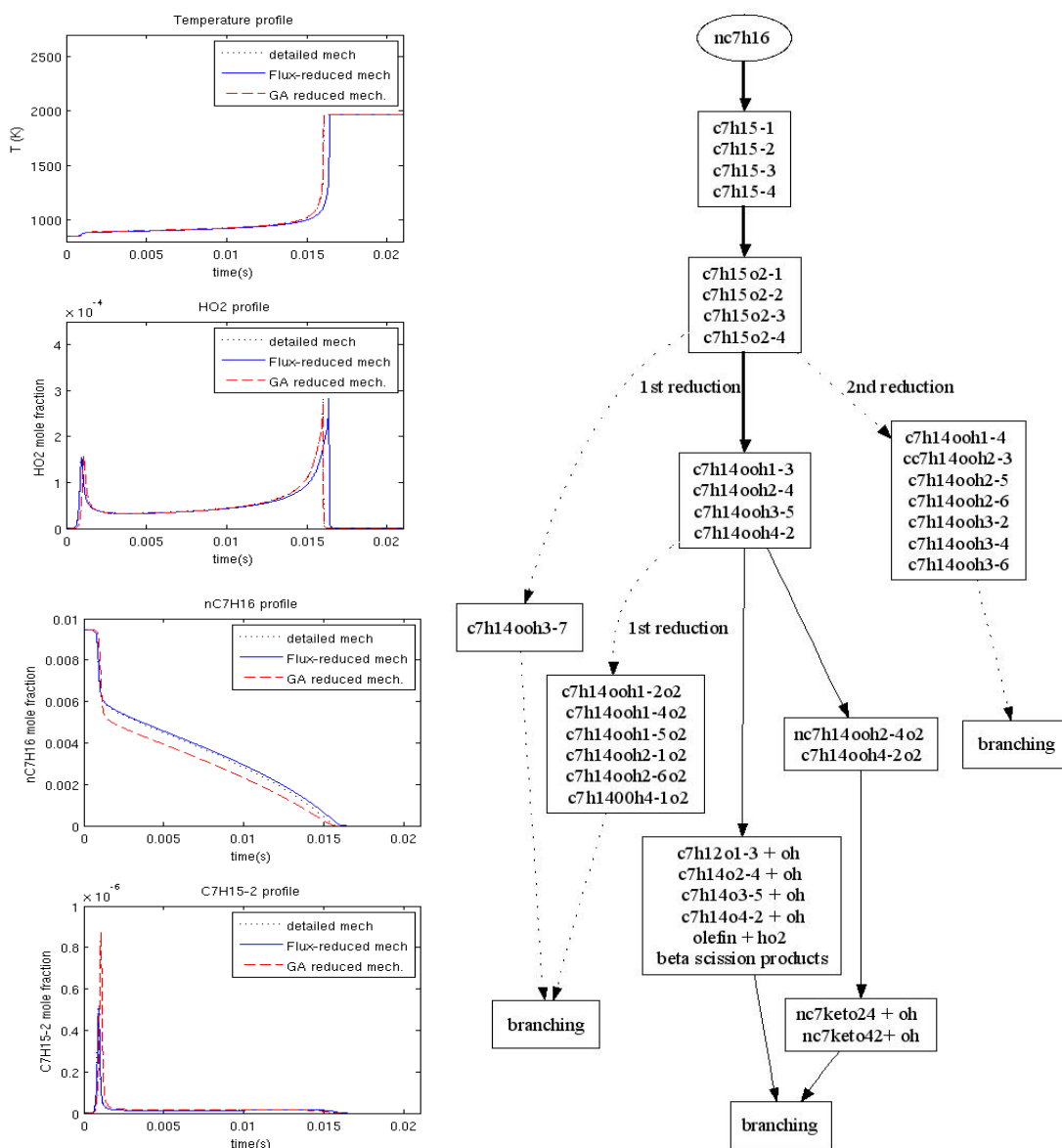
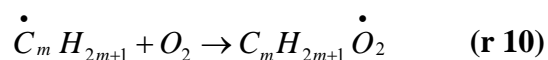


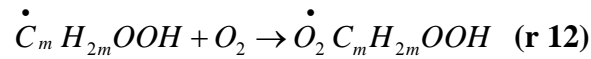
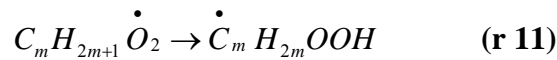
Figure 10.c: NTC temperature oxidation (850 K) of fuel lean of n-C7H16 – air mixture (equivalence ratio = 0.5. The detailed mechanism has 561 species and 2539 reactions. The flux-reduced mechanism consists of 260 species and 1215 reactions. The GA reduced mechanism contains 160 species and 731 reactions. Temperature profile and species profiles are on the left. Reaction pathway diagram is on the right.)

- **Low temperature oxidation of n-heptane oxidation**

The diminutions of n-heptane – air mixture at low temperature oxidation were carried out at 550 K for fuel rich, stoichiometric, and fuel lean mixture. Figure 11 depicts temperature and some species profiles and reaction pathway diagrams of the detailed mechanism, the flux reduced mechanism, and the GA reduced mechanism. As shown on the left hand sides of figure 11, the profiles of the flux-reduced mechanism predict combustion at low temperature with great accuracy. Although the GA reduction eliminated over 41% species in fuel rich, 35% species in stoichiometric and fuel lean mixture; and thus ultimately disabled 55% reactions in fuel rich, 57% reactions in stoichiometric and 45% reaction in fuel lean mixture from the flux-reduced mechanism, the GA reduced mechanisms can capture very well the behavior of the system at low temperature for all considering conditions.

At low temperature, the activation energy of β -scissor reactions of alkyl radicals is very high, these reaction channels become less important (Curran *et al.*(1998a)). Since activation energy associated with oxygen addition to alkyl radical is zero, oxygen reacts with heptyl radicals to generate hydroperoxide-heptyl radicals ($\dot{C}_7H_{14}OOH$). Yet, low temperature does not support the dissociation of $\dot{C}_7H_{14}OOH$. It makes way for the 2nd oxygen addition to form $\dot{O}_2C_7H_{14}OOH$ compounds leading to the generation of keto compounds. They quickly decompose further to generate another OH radical, carbonyl compounds as following:





These channels continue branching and increasing the oxidation rate. They are responsible for the formation of cool flames (Androulakis (2004)).

The reaction pathway diagrams are shown on the right hand sides of figure 11. The thickness of the lines indicates the amount of carbon flux transferring through these reaction pathways. The solid lines are the pathways remaining in final reduced mechanism. The dotted lines, assigned with 1st reduction or 2nd reduction, are the reaction pathways, which were eliminated by the flux analysis or the GA reduction. As shown in figure 11a, 11b, and 11c, all channels from $\dot{C}_7 H_{14} OOH$ depict the low temperature chemistry. Those species that have accumulated element flux smaller than cut-off threshold are eliminated by the flux reduction step. They are the dotted lines on the left part of diagrams and assigned with 1st reduction. The other dotted lines, which are on the right part of the diagrams and labeled with 2nd reduction, are the reaction pathways eliminated by the GA reduction.

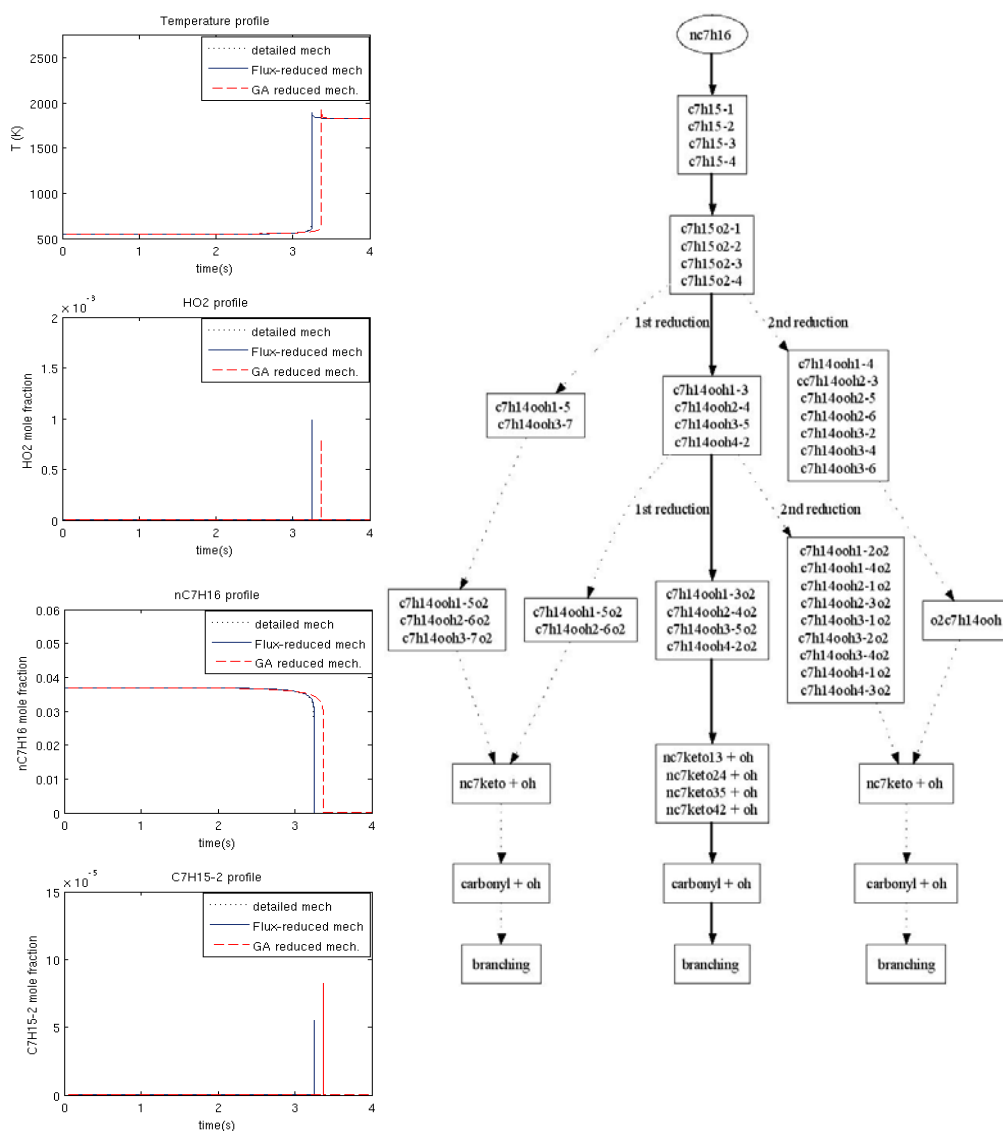


Figure 11.a: Low temperature oxidation (550 K) of fuel rich of n-C7H16 - air mixture (equivalence ratio = 2.0. The detailed mechanism has 561 species and 2539 reactions. The flux-reduced mechanism consists of 275 species and 1406 reactions. The GA reduced mechanism contains 162 species and 632 reactions. Temperature profile and species profiles are on the left. Reaction pathway diagram is on the right.)

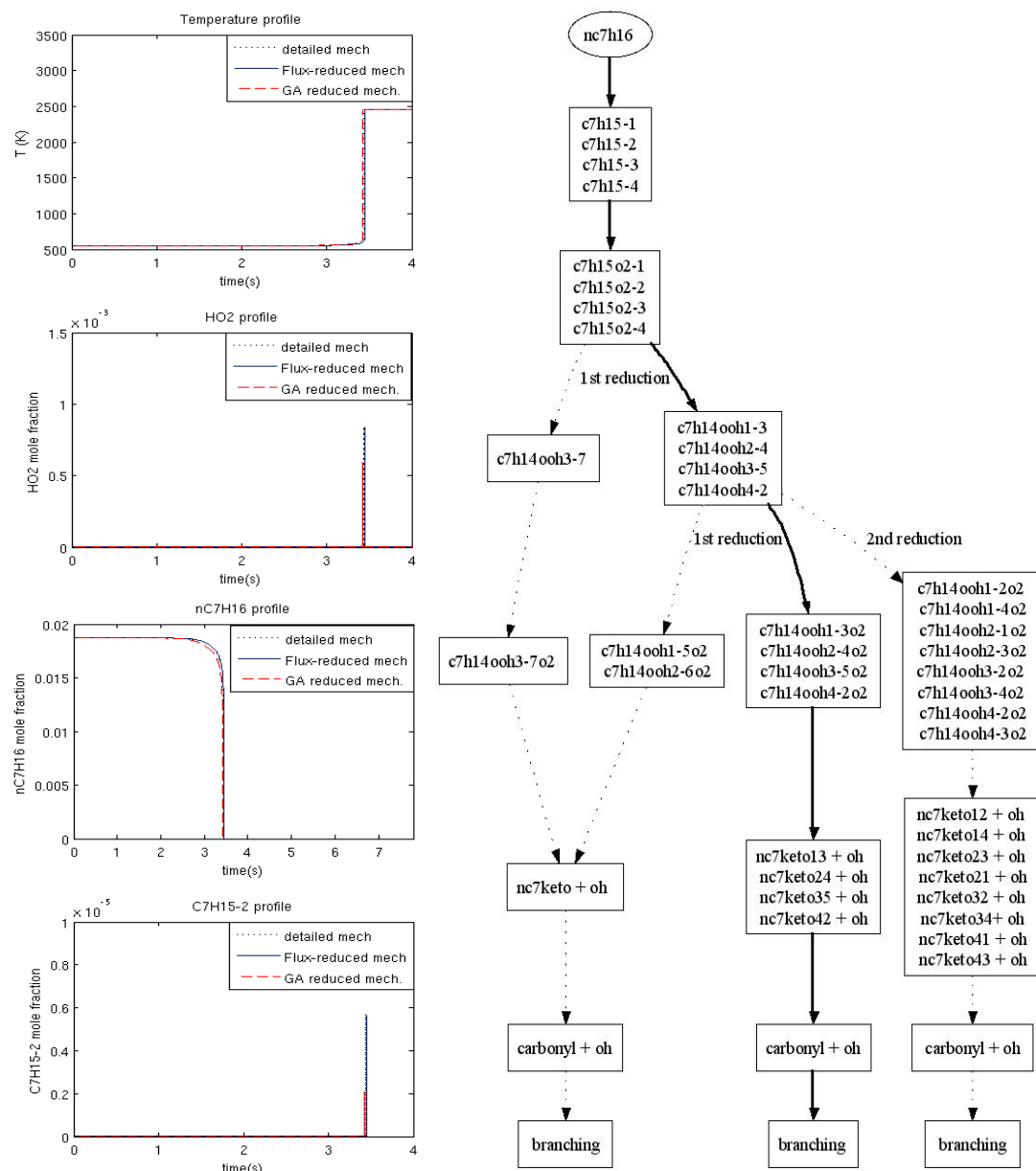


Figure 11.b: Low temperature oxidation (550 K) of stoichiometric n-C₇H₁₆ – air mixture (equivalence ratio = 1.0. The detailed mechanism has 561 species and 2539 reactions. The flux-reduced mechanism contains 278 species and 1338 reactions. The GA reduced mechanism consists of 171 species and 585 reactions. Temperature profile and species profiles are on the left. Reaction pathway diagram is on the right.)

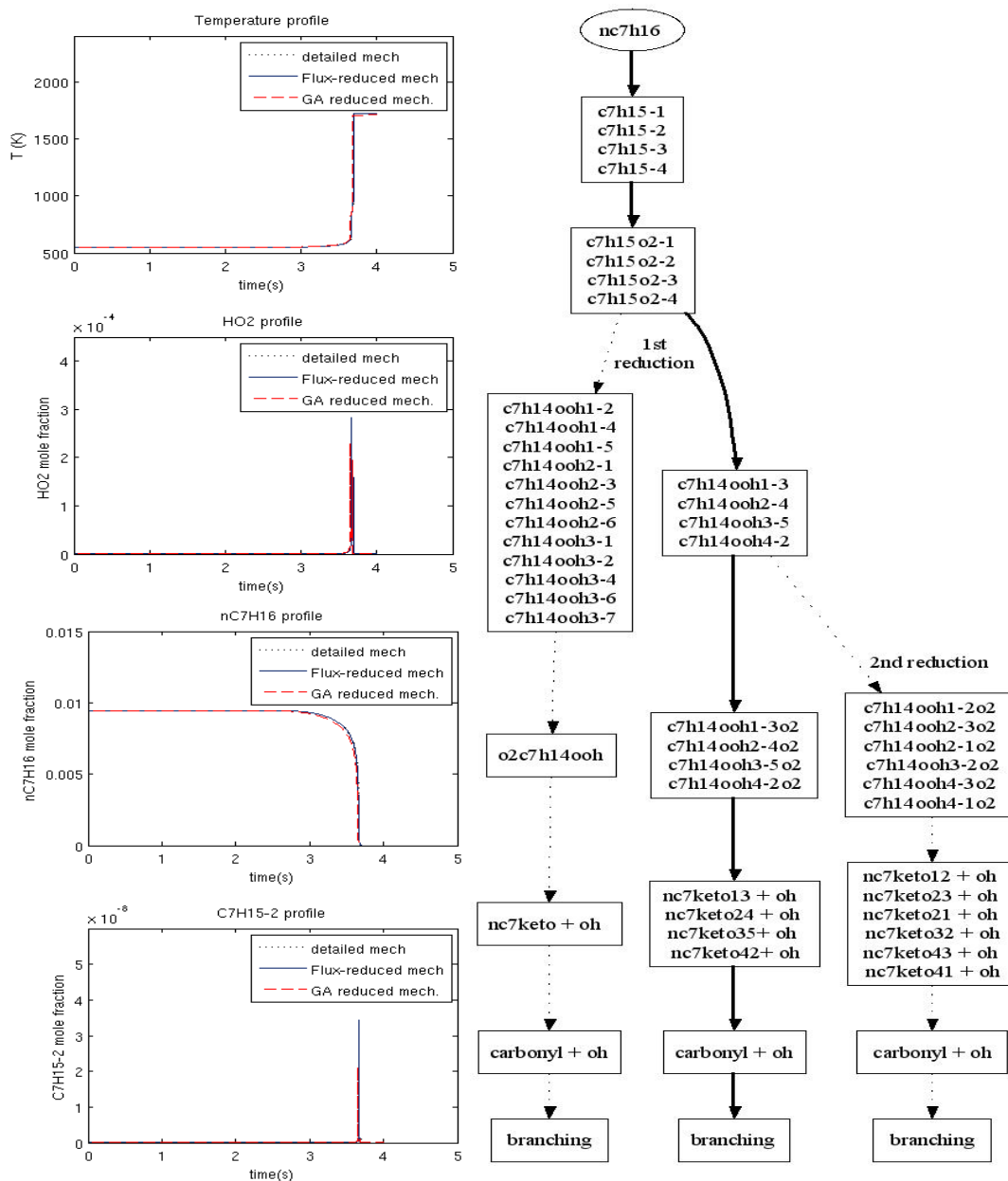


Figure 11.c: Low temperature oxidation (550 K) of fuel lean of n-C₇H₁₆ – air mixture (equivalence ratio = 0.5. The detailed mechanism has 561 species and 2539 reactions. The flux-reduced mechanism contains 271 species and 1193 reactions. The GA reduced mechanism consists of 178 species and 657 reactions. Temperature profile and species profiles are on the left. Reaction pathway diagram is on the right.)

3.3. Autoignition delay simulation with reduced mechanisms of n-pentane and n-heptane

Autoignition delay is a fundamental characteristic of fuel combustion. It details the requirement time for a considered fuel – air mixture to ignite at a given temperature and pressure. Several studies have been carried out on rapid compression machine (RCM). The mixture is quickly compressed to reach the initial pressure then ignites itself. The corresponding initial temperature is estimated as the adiabatic compression temperature. Minetti *et al.* (1995) did experiment on a RCM machine and recorded the autoignition delay of n-C₅H₁₂ – air and n-C₇H₁₆ – air mixture in a wide range of temperature for the mean compressed charge density 135.5 mol m⁻³. They also simulated the autoignition delay of these fuels with detailed mechanism and used their experiment results to verify the detailed mechanisms. F. Maroteaux and L. Noel (2006) modeled the combustion of n-C₇H₁₆ using their reduced mechanisms. We are interested in applying our reduced mechanisms to replicate the autoignition delay of n-C₅H₁₂ – air mixture and n-C₇H₁₆ – air mixture.

In our simulation, the considered mixture was modeled with a constant volume combustion process at initial conditions of compression pressure. The mixture was permitted to ignite at these conditions and ignition time was recorded. We assume that, a mixture starts to ignite when 50% amount of requirement oxygen is consumed. For example, the ignition time of the stoichiometric mixture of n-C₅H₁₂ and air is the time at which the concentration of oxygen in the mixture is 50% of that at initial. The n-pentane autoignition delay of stoichiometric – air mixture given by detailed mechanism, a reduced mechanism with 75 species, and experiments done by Minetti and co-workers

(1995) was shown in the work of Androulakis (2004). In this work, the autoignition delay of the detailed mechanism of n-C₅H₁₂ and n-C₇H₁₄ was used as a reference. Because the reduced mechanisms were obtained by removing the eliminated species from detailed the mechanism of Curran *et al.* (1998), any combination of reduced mechanisms can introduce some unwanted reactions. Therefore, the reduced mechanisms at low temperature were applied when initial temperature is in low temperature range, the reduced mechanisms at NTC temperature were used at NTC temperature range, and ones at the high temperature were functioned at high temperature range. For instance, the low temperature range starts at 600 K and ends at 740 K, the NTC temperature range begins at 740K and ends at 1000 K, and the range from 1000 K on is high temperature for n-C₅H₁₂ – air combustion. Figure 12 presents the autoignition delay simulation of nC₅H₁₂ – air and n-C₇H₁₆ – air mixture and the lag time error of the GA reduced mechanisms and the flux-reduced mechanisms. As can be seen in figure 12, the flux-reduced mechanisms capture the autoignition delay of considered mixture greatly and GA reduced mechanisms estimate the ignition time very well. Most of the calculated autoignition errors are less than 10% while the calculation time of adaptive scheme is 65% smaller than that of using detailed mechanism.

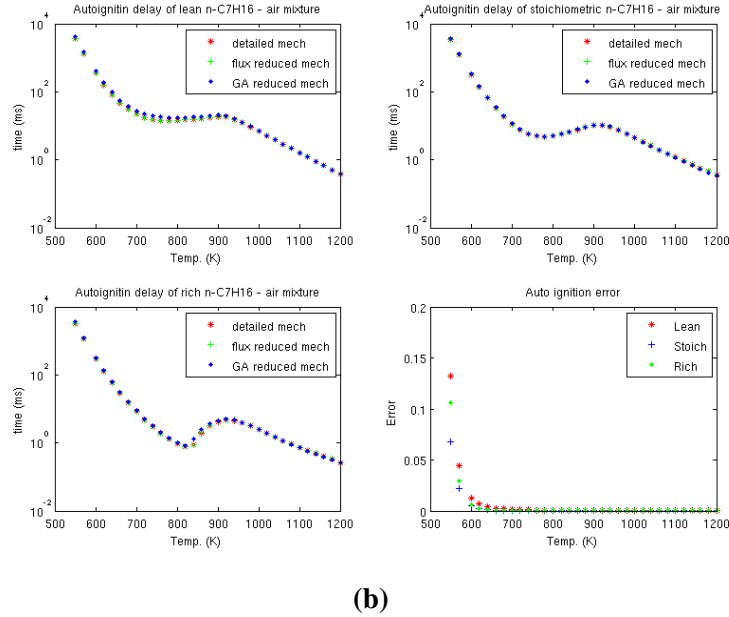
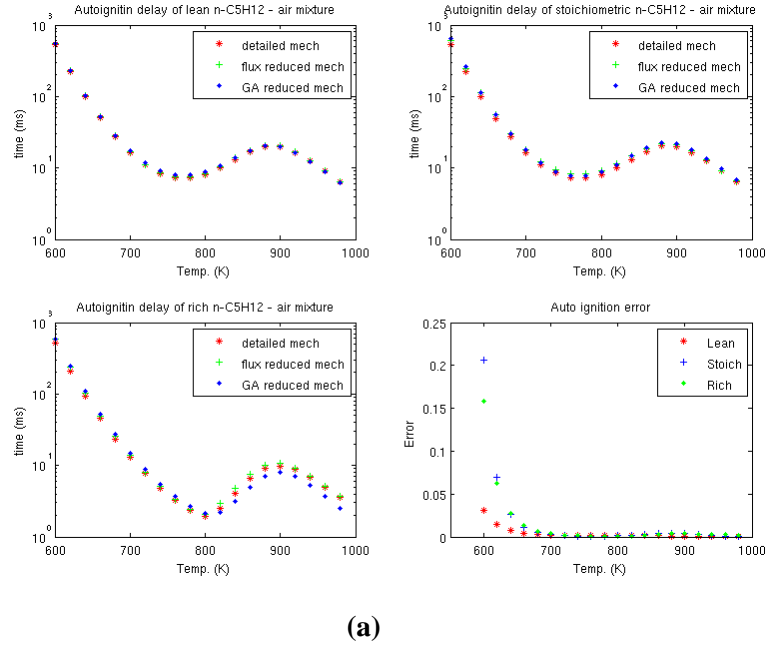


Figure 12: Autoignition delay simulation with the detailed mechanism, the flux-reduced mechanism, and the GA reduced mechanisms of fuel – air mixture for mean compressed charge density 135.5 mol m^{-3} . (Asterisk mark detailed mechanism, plus mark flux-reduced mechanisms, and diamond mark GA reduced mechanisms. (a) n-C5H12 is at the top, and (b) n-C7H16 is at the bottom)

3.4. Summary

In this work, we combined the approach of flux analysis and mathematical programming method to form a two-step reduction approach and applied on very complex mechanisms. The flux analysis was used as the first step to truncate the search space of the mathematical programming as well as a tool for exploring the reaction pathways. We investigated nine conditions of n-pentane and nine conditions of n-heptane to obtain 18 reduced mechanisms (nine for each kind of fuel). These reduced mechanisms have much less number of species and reactions than those of detailed mechanism with an acceptable error. The reaction pathway analysis reveals the complex chemistry of the combustion system. It is very interesting that the fuel rich mixture of n-C₅H₁₂ – air mixture tends to behave like high temperature oxidation at low temperature. This tendency also becomes dominant at NTC for fuel rich mixture. The low temperature chemistry seems to dominate fuel lean n-C₅H₁₂ – air mixture at NTC. We also observe high temperature chemistry channels in fuel rich mixture oxidation at NTC. Nonetheless, they are not as strong as they are in the case of n-pentane. The low temperature chemistry channels still remain in stoichiometric and fuel lean mixture oxidation of n-heptane at NTC. However, their influence is not important as in the oxidation of n-pentane. The obtaining reduced mechanisms of n-C₅H₁₂ and n-C₇H₁₆ serve as an adaptive chemistry scheme in auto ignition delay model of fuel – air at 135.5 mol m⁻³ charge density. The simulation shows that the error coming from adaptive scheme is acceptable while CPU time of adaptive scheme is much smaller than that of using detailed mechanism.

Chapter IV SUMMARY AND FUTURE WORK

The two-state reduction method is successful in finding a good reduced mechanism. The flux analysis gives a global view of the element transformation in a mechanism. Based on a suitable cut-off threshold, the detailed mechanism of n-C₅H₁₂ and n-C₇H₁₄ oxidation was truncated to form 18 flux-reduced mechanisms (nine for each fuel). Although the selected thresholds were small, the flux analysis eliminated a large number of species and indirectly disabled so many reactions from the concerned detailed mechanism. The GA search was applied in the second reduction step to solve a mixed integer nonlinear optimization. It further removed some unimportant species from the flux-reduced mechanisms. The success of this method opens a novel way for building reduced mechanisms, which are very useful for CFD calculation not only in combustion simulation but also in the modeling of bio-systems. The analysis of the reaction channels in the considered mechanism revealed that the fuel rich mixture tends to behave as high temperature oxidation while the fuel lean mixture acts like low temperature oxidation. As mentioned in the work of Banerjee (2006), the obtaining reduced mechanisms also contain some redundant reactions that can be further removed by applying reaction reduction. The procedure of reaction reduction using GA is similar to species reduction. Nonetheless, the reactions are encoded to form a chromosome instead of species as they are in this work. There are some related concerns that need to be investigated in the future such as

- The objective function of the considering optimization was built on temperature and species. While the species selection is based on the users' viewpoint, therefore, it is different from one to another. As a result, it requires a new variable, which can better characterize the system or a method that can define important factors for an initial oxidation condition.
- Since a reduced mechanism can work well in a limited condition, it requires a library of reduced mechanisms to simulate combustion. This mission opens an adaptive chemistry problem done very well for combustion of methane in the work of Banerjee (2006) on Temperature – fuel – oxygen space. However, this space may not be able to characterize the process of complicated mechanism such as n-C₅H₁₂ or n-C₇H₁₆ oxidation. Furthermore, the point-in-polygon algorithm in the Banerjee's work is an expensive. It may not be economic to apply for a multi-dimension space. The adaptive scheme for complex mechanism needs another classifier to select a suitable reduced mechanism.

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