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Directed Relation Graph with Expert Knowledge for Skeletal Mechanism Reduction

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The directed relation graph (DRG) method for skeletal mechanism reduction was extended to accommodate expert knowledge on chemical kinetics in skeletal mechanism reduction. The expert individually specifies the reduction error for any species such that the species associated with reaction pathways known to be important are retained with high accuracy. Otherwise a species is allowed to have larger reduction error by default. Thus, for the same reduction error tolerance on a given combustion parameter (e.g., ignition delay) and/or species concentrations, the DRG with expert knowledge (DRGX) can generate smaller skeletal mechanisms than those generated using the conventional DRG method by allowing smaller reduction errors for heat release or species of interest while allowing larger errors for other species. The DRG and DRGX methods were then compared using detailed mechanisms of *n*-dodecane and a tri-component biodiesel surrogate. The mechanisms derived with DRGX feature overall higher accuracy than those derived with DRG using the same error tolerance, while the computational costs for the reduction are nearly identical for the two methods. The resulting skeletal mechanisms were validated in different systems involving ignition and extinction.

1. Introduction

Practical engine fuels involve large hydrocarbons with complex molecular structures. For example, *n*-dodecane is an important surrogate component for diesel and jet fuels [1], and methyl decanoate (MD) and other long chain fatty acid methyl esters (FAME) were found to be good surrogates for biodiesel [2]. The oxidation of long chain molecules involves many intermediate species and reaction pathways, as such their detailed chemical kinetic mechanisms are highly complex, frequently consisting of thousands of species and even more reactions [2-5]. These large detailed mechanisms are difficult to include in practical engine simulations, and can even be difficult to use for chemical kinetic analysis in 0-D and 1-D systems. Therefore, mechanism reduction is important for studying detailed chemical kinetic mechanisms of practical engine fuels.

Skeletal reduction is an important method for mechanism reduction that eliminates unimportant species and reactions from detailed mechanisms. Skeletal reduction can be achieved using such methods as sensitivity analysis [6], detailed reduction [7], principal component

analysis [8], Jacobian analysis [9], directed relation graph (DRG) [10-13], DRG with error propagation (DRGEP) [14, 15], DRG aided sensitivity analysis (DRGASA) [16, 17], DRGEP and sensitivity analysis [18], and path flux analysis [19]. The DRG method features a linear time algorithm and is particularly suitable for the reduction of extremely large mechanisms. The DRG method requires as input one or more major species as the search-imitating species, in addition to a user-specified error tolerance that uniformly limits the reduction error for all the species in the resulting skeletal mechanism. While such a uniform error control renders the DRG method simple to apply, it nonetheless results in the lack of flexibility in tailoring the skeletal mechanisms based on the uneven uncertainties in various reaction pathways in large detailed mechanisms.

In the present study, the DRG method is extended to allow species-specific error tolerances in the reduction. Such expert-specified species-specific information renders it possible to develop a skeletal mechanism that is highly accurate for heat release or species concentrations of interest, while at the same time retaining moderate accuracies for other species in the skeletal mechanism.

2. Methodology

The method of DRG is based on the observation that many species are only weakly coupled during combustion processes, such that the species that do not significantly affect the reaction rates of the major species can be eliminated from the mechanism. The first step in DRG is to quantify species coupling by the pair-wise error, r_{AB} , induced to a species A by the elimination of another species B for a given reaction state that consists of temperature and the species concentrations [10, 13]:

$$r_{AB} \equiv \frac{\max_i |\nu_{A,i} \omega_i \delta_{Bi}|}{\max_i |\nu_{A,i} \omega_i|}, \quad \delta_{Bi} = \begin{cases} 1, & \text{if the } i\text{th reaction involves } B \\ 0, & \text{otherwise} \end{cases}, \quad (1)$$

where ω_i is the net reaction rate of the i^{th} reaction and $\nu_{A,i}$ is the stoichiometric coefficient of species A in the i^{th} reaction. It is seen that the denominator in eq.(1) indicates the largest reaction rate that contributes to the production rate of species A , while the numerator indicate the largest reaction rate contributing to A that also involves species B . Therefore, a small r_{AB} indicates that none of the reactions involving B is important to the production of species A , i.e. species B is considered unimportant to A . Otherwise B is important to A and will be retained in the skeletal mechanism if A is to be retained.

The species dependence defined based on eq. (1) can then be expressed in the following graph notation

$$A \rightarrow B \text{ iff } r_{AB} > \varepsilon, \quad (2)$$

i.e. there is a directed edge from species A to B if and only if r_{AB} is larger than a user specified threshold error. The vertices in the DRG are the species in the detailed mechanism, and the adjacency matrix, \mathbf{E} , of the digraph is defined as:

$$E_{ij} = \begin{cases} 1, & \text{if } r_{ij} > \varepsilon \\ 0, & \text{if } r_{ij} \leq \varepsilon \end{cases} \quad (3)$$

Starting from one or more species of interest, such as the H radical, a revised depth-first search (RDFS) [12] was employed to obtain the threshold error for each species to be eliminated. It is noted that for the DRG reduction a set of reaction states need to be sampled from combustion

problems of interest. The final skeletal mechanism derived using DRG consists of all the species and reactions that should be retained for any of the sampled reaction states.

The DRG method features overall linear reduction time and was fully automated for the reduction of large mechanisms. It was confirmed in the reduction of various detailed mechanisms that the measured reduction error can be effectively controlled by the user-specified threshold error, ϵ , [20]. Moreover, every species in a skeletal mechanism derived with DRG is limited by the same error tolerance, such that the skeletal mechanisms from DRG feature high chemical fidelities if a small ϵ , say 0.1, is used. It was found that an ϵ larger than 0.15 may result in unsafe elimination of important species in large mechanisms for engine fuels. An improved definition of r_{AB} in eq. (1) can allow threshold values of up to 0.4 in the reduction of engine fuels such as biodiesel [21]. Nevertheless, a limiting issue remains in the DRG method, that is, the reduction error was uniformly specified for all species. As such it is not possible in DRG to allow a large overall reduction error and at the same time enforcing the accurate prediction of heat release or of selected species concentrations, although this is important in kinetic studies if there are significantly disparate uncertainties in the detailed mechanism. As a result, if the skeletal mechanism needs to be highly accurate for prediction of heat release or a few species of interest, only a very small threshold error can be specified in the reduction and the reduction extent will be rather limited. To resolve this problem, expert knowledge can be included in the extended DRG reduction.

Procedurally, in addition to the starting species, e.g., the H radical, species-specific x -values, i.e., the expert knowledge, are specified for selected species. A species, A , associated with reactions with small uncertainties can be assigned a small x -value, say $x_A=0.1$, and that with larger uncertainties can be assigned a larger x -value, say $x_A=0.3$. Any species B with $r_{AB} > x_A$ will be retained in the skeletal mechanism, while other species are treated with the original DRG reduction using a default error tolerance, say $\epsilon=0.5$. As a result, the errors in the skeletal mechanisms roughly match the level of uncertainties in the detailed mechanisms, such that the overall chemical fidelity can be retained. Moreover, for applications where some species of interest, e.g., a pollutant, need to be predicted with higher accuracy than the other species, small x -values can also be specified. The x -values can either be pre-processed or post-processed in DRGX. A pseudo code of the DRGX method, extended from that in Ref. [12], is provided in Fig. 1.

It is seen from the pseudo code that the pre-processing of the x -values is to expand the starting species set in the previous DRG method, and the post-processing of the x -values is to retain the species that are important to a species A based on its assigned x -value x_A . It can be shown that the ϵ values computed in DRG and DRGX for a species A are always in the order of

$$\epsilon_{DRG} \leq \epsilon_{DRGX, post-processing} \leq \epsilon_{DRGX, pre-processing} \quad (4)$$

Therefore, by specifying the same threshold error, ϵ , the DRG method results in the smallest mechanism, and the DRGX with pre-processing of expert knowledge results in the largest mechanism. As such pre-processing the x -values is a rather conservative option for DRGX. It can be used when chemical fidelity is the primary concern. In the present study, DRGX with post-processing was found to be a good option in deriving a skeletal mechanism with balanced size and chemical fidelity. It is further noted that to include the x -value for heat release in DRGX, it simply needs to treat heat release as a special species Q , with $\nu_{Q,i}$ being the reaction

heat for the i th reaction. For example, $x_Q = 0.1$ can be specified if the error in heat release for the skeletal mechanism should be smaller than about 10%.

DRGX

```

For each reaction  $i = 1:I$ 
  For each species pair  $A, B$  involved in reaction  $i$ ,
    If edge  $A \rightarrow B$  is not initialized
      Initialize edge  $A \rightarrow B$ 
       $r_{AB} = 0$ 
       $r_{A,max} = 0$ 
    End if
     $r_{AB} = \max(r_{AB}, |v_{A,i} \omega_i|)$ 
     $r_{A,max} = \max(r_{A,max}, |v_{A,i} \omega_i|)$ 
  End for
End for
For each initialized edge
   $r_{AB} = r_{AB} / r_{A,max}$ 
End for

```

```

If pre-processing the expert knowledge in DRGX
  For each species  $A$  with expert knowledge  $x_A$ 
    Add species  $A$  in the set of starting vertices
    For each species  $B$  with  $r_{AB} > x_A$ 
      Add species  $B$  in the set of starting vertices
    End for
  End for
End if

```

Call RDFS()

```

If post-processing the expert knowledge in DRGX
  For each species  $A$  with specified expert knowledge  $x_A$ 
    Mark species  $A$  with the value 1
    For each species  $B$  with  $r_{AB} > x_A$ 
      Mark species  $B$  with the value 1
    End for
  End for
End if

```

Eliminate species with marked values smaller than ε and any reactions involving the eliminated species
 Write the retained species and reactions to the skeletal mechanism

End

RDFS()

```

Truncate the  $r_{AB}$  values based on the number of buckets and bucket sort the edges in descending order of  $r_{AB}$ 
Initialize an empty graph with only vertices
Mark the starting vertices with unity and the other species with zero
For each edge  $A \rightarrow B$  in the sorted list
  Insert  $A \rightarrow B$  into the graph
  If  $A$  is marked and  $B$  is not marked
    Depth-first search with  $B$  as root, mark every newly discovered vertex with value  $r_{AB}$ 
  End if
End for

```

End

Figure 1. A pseudo code for the DRGX method

3. Results and Discussion

3.1 Reduction of a detailed *n*-alkane mechanism

The performance of the DRGX method is first investigated with auto-ignition of a stoichiometric mixture of *n*-dodecane–air at constant pressure of 10 atm and initial temperature of 850 K using a detailed mechanism for C₈–C₁₆ *n*-alkanes from Lawrence Livermore National Laboratory (LLNL) [5] to compare DRG and DRGX with pre- and post-processing options. The detailed mechanism consists of 2115 species and 8157 reactions.

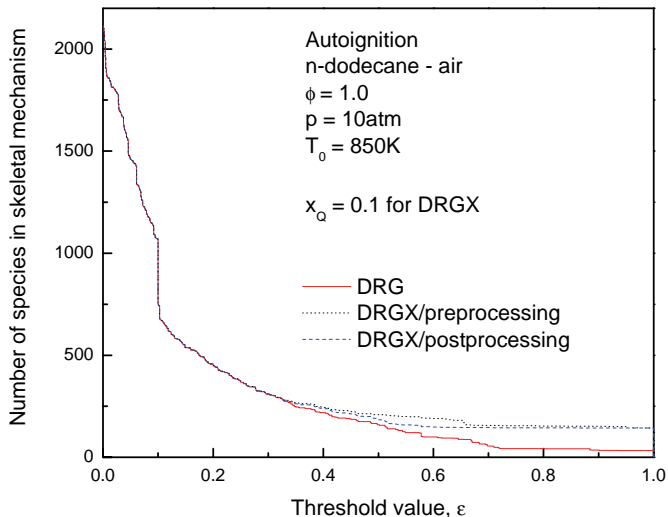


Figure 2. Reduction curves for DRG, DRGX with pre- and post-processing options, respectively, with $x_Q = 0.1$ in DRGX for auto-ignition of stoichiometric *n*-dodecane–air at pressure of 10atm and initial temperature of 850K.

Figure 2 shows the reduction curves of the three different approaches. For the DRGX reductions, $x_Q = 0.1$ was specified for heat release. It is seen that for small threshold errors, say $\epsilon < 0.2$, the reduction curves for the three different methods collapse, while for larger threshold values, say $\epsilon > 0.4$, DRGX with pre-processing results in the largest mechanisms and DRG yields the smallest as discussed in eq. (2). It is further seen that the reduction curves feature steep slopes for small threshold values, indicating that large extent of reduction can be achieved with small reduction errors. It is further seen that the reduction curves for DRGX become almost plateaus when the threshold value is large, say $\epsilon > 0.7$. This is because the set of species important for heat release are retained due to the small x_Q , such that few species can be further eliminated by increasing the threshold value ϵ .

Figure 3a shows the temperature profiles predicted using different skeletal mechanisms derived with the three approaches with different threshold errors. By specifying a small threshold error $\epsilon = 0.2$, the three different methods resulted in the same skeletal mechanism with 449 species, and the temperature profile of the 449-species mechanism closely agrees with that of the detailed mechanism. This shows that for very small ϵ values, DRGX reduces to DRG. By increasing the threshold error to $\epsilon = 0.5$, which is a rather aggressive value for the DRG-based methods, three skeletal mechanisms with 160, 208, and 184 species were obtained using DRG,

DRGX/pre-processing and DREGX/post-processing, respectively. It is seen that the overall error is quite large for the DRG-derived mechanism, while the mechanism from DREGX/pre-processing has a much smaller error in post-ignition temperatures. Figure 3b further shows the effect of changing x_Q on the accuracy of the resulting mechanism. It is seen that for a fixed threshold error $\epsilon=0.5$, by decreasing x_Q from 0.1 to 0.01, the resulting skeletal mechanism expanded to 368 species and the accuracy in temperature is substantially improved. The effects of different x -values and the ϵ values on the size and accuracy of the resulting skeletal mechanisms for DRG and DREGX is therefore demonstrated.

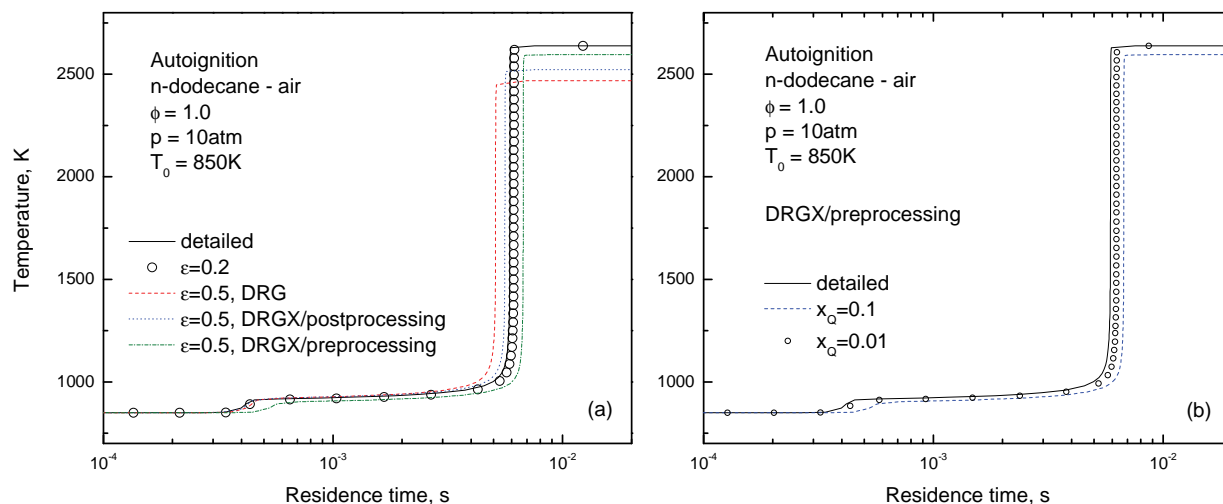


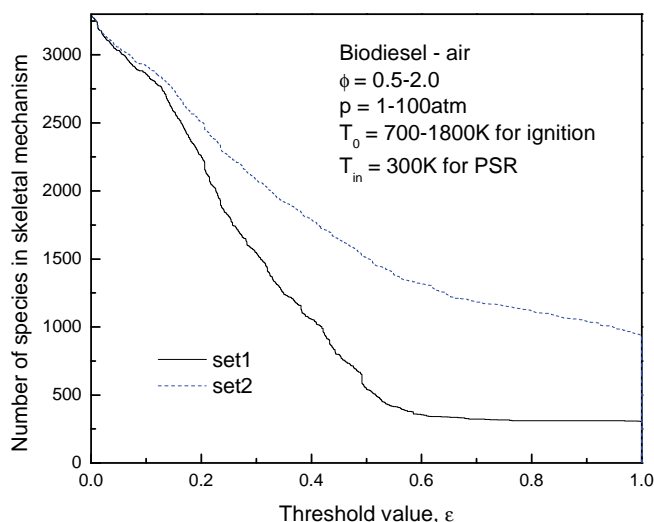
Figure 3. Comparison of the accuracy of the skeletal mechanisms derived with a) DRG, DREGX/pre-processing and DREGX/post-processing with different threshold errors with $x_Q = 0.1$, and b) DREGX/pre-processing with different x_Q , for auto-ignition of stoichiometric *n*-dodecane-air mixture at pressure of 10atm and initial temperature of 850K.

3.2 Reduction of a detailed tri-component biodiesel surrogate mechanism

DREGX/post-processing is then applied to reduce the detailed mechanism from LLNL for a tri-component surrogate mixture of biodiesel [2], comprised of 25% MD, 25% methyl-9-decenoate (MD9D), and 50% *n*-heptane in mole. The detailed mechanism consists of 3299 species and 10,806 reactions. The target for the present reduction is to derive a comprehensive and accurate skeletal mechanism using DREGX over the parameter range of pressure from 1 to 100 atm, equivalence ratio from 0.5 to 2.0, and ignition temperature from 700 to 1800K for auto-ignition. Extinction in perfectly stirred reactions (PSR) was also included in the reduction. The reduction was based on more than 21,000 reaction states sampled from auto-ignition and PSR. It took less than about 10 minutes using 100 CPU cores for each DREGX reduction in parallel configuration. Two sets of expert knowledge were used in the reduction. In Set 1, only the x -values from heat release and the H radical was set, specifically $x_Q=0.1$, and $x_H = 0.3$. In Set 2, in addition to $x_Q=0.1$, x -values were further specified for the species listed in Table 1. It is noted that while the x -values in Set 1 can be used to obtain smaller mechanisms that is good to predict the overall system parameters such as ignition delays and extinction time, the x -values in Set 2 can be used to obtain skeletal mechanisms with high chemical fidelity, for such purposes as detailed reaction pathway analysis.

Table 1. Species and the corresponding x-values for the reduction of the detailed mechanism for surrogate mixtures of biodiesel using DRGX.

MD	(0.1)	MB3D	(0.3)	C5H11-1	(0.2)	MD9D2OOH4J	(0.3)
MD9D	(0.1)	OH	(0.1)	PC4H9	(0.2)	MD9D2OOH5J	(0.3)
NC7H16	(0.1)	H	(0.1)	NC3H7	(0.2)	MD9D3OOH5J	(0.3)
O2	(0.1)	CH3	(0.1)	MP2D3J	(0.2)	MD9D3OOH5J	(0.3)
H2	(0.1)	CH3O	(0.2)	MB3D4J	(0.2)	C7H14OOH2-4	(0.3)
H2O	(0.1)	C2H5	(0.2)	MD2O2	(0.3)	C7H14OOH2-5	(0.3)
CO	(0.1)	MD2J	(0.1)	MD3O2	(0.3)	C7H14OOH3-5	(0.3)
CO2	(0.1)	MD3J	(0.2)	MD9D2O2	(0.3)	C7H14OOH3-6	(0.3)
CH4	(0.2)	MDMJ	(0.3)	MD9D3O2	(0.3)	C5H10-1	(0.3)
C2H4	(0.2)	MD9D2J	(0.1)	C7H15O2-2	(0.3)	C6H12-1	(0.3)
C2H2	(0.2)	MD9D3J	(0.2)	C7H15O2-3	(0.3)	C7H14-1	(0.3)
C3H6	(0.2)	MD9DMJ	(0.3)	MD2OOH4J	(0.3)	C8H16-1	(0.3)
C4H8-1	(0.3)	C7H15-1	(0.2)	MD2OOH5J	(0.3)	C8H14-17	(0.3)
C4H6	(0.3)	C7H15-2	(0.1)	MD2OOH5J	(0.3)	C7H12-16	(0.3)
CH2O	(0.3)	C7H15-3	(0.1)	MD3OOH5J	(0.3)	C6H10-15	(0.3)
MP2D	(0.3)	C6H13-1	(0.2)	MD3OOH6J	(0.3)	C5H8-14	(0.3)

**Figure 4. Reduction curves for biodiesel-air using DRGX/post-processing with two different sets of x-values.**

The reduction curves of DRGX using the two different sets of x-values are shown in Fig. 4. It is seen that the reduction curve for Set 1 is steeper than that for Set 2 due to the additional high accuracy requirements for the species in Table 1. Consequently, by specifying a threshold error of $\epsilon=0.5$, a 540 species skeletal mechanism (sk540) was obtained for Set 1, and a 1504 species mechanism (sk1504) was obtained for Set 2. The two skeletal mechanisms are then validated with the detailed mechanism for auto-ignition and extinction in PSR. It is seen in Fig. 5 that both skeletal mechanisms agree quite well with the detailed mechanism within the entire parameter range of the validation, while the errors of sk540 is overall larger than that of sk1504 for both ignition and extinction of lean mixtures under high pressure. It is noted nevertheless that, being substantially larger than sk540, sk1504 is not only more accurate in predicting heat release, but also features higher chemical fidelity for many species as specified in Table 1.

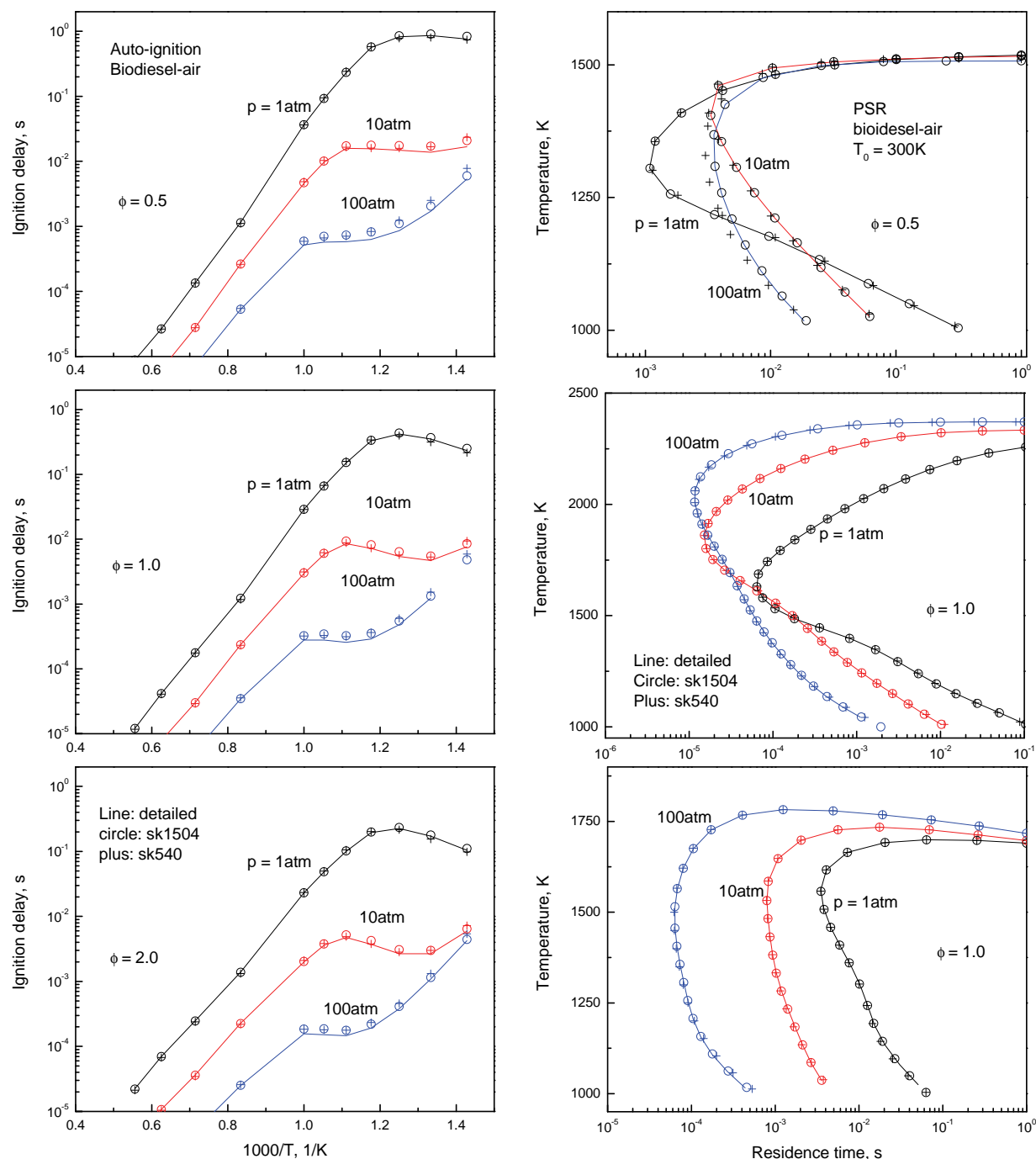


Figure 5. Validation of the skeletal mechanisms (sk504 from Set 1 and sk1504 from Set 2) derived using DRGX/post-processing for auto-ignition and PSR within the parameter range of the reduction.

To further shown the difference of chemical fidelities between the two skeletal mechanisms, Figure 6 compares the species concentrations calculated by the detailed and the skeletal mechanisms, respectively. Fig. 6a shows the concentrations of selected major species including MD, CO and CO_2 , which are important for heat release. It is not surprising that both skeletal mechanisms agree closely with the detailed mechanism for these major species, because the

same $x_Q=0.1$ was specified to obtain both skeletal mechanisms. However, larger differences were observed in Fig. 6b for intermediate species such as H, CH₃ and C₂H₂. This is consistent to the fact that rather small x-values were specified for sk1504 ($x_H = 0.1$, $x_{CH_3}=0.1$, and $x_{C_2H_2}=0.2$) while larger errors were specified for sk540 ($x_H = 0.3$, and $\epsilon=0.5$ by default for CH₃ and C₂H₂). Therefore, while sk540 as a smaller mechanism can be more suitable for practical engine simulations after further reduction, sk1504 may be better for chemical kinetic analysis requiring high accuracies in detailed reaction pathways for the species listed in Table 1. A potential application of such an approach would be to use the smaller mechanism in a 3-D CFD simulation to identify conditions (e.g., temperatures, pressures, mixture fractions, etc.) of important regions in the phase-space, and then model these conditions using the larger mechanism in a less computationally expensive 0- and 1-D simulation to delineate the important reaction pathways.

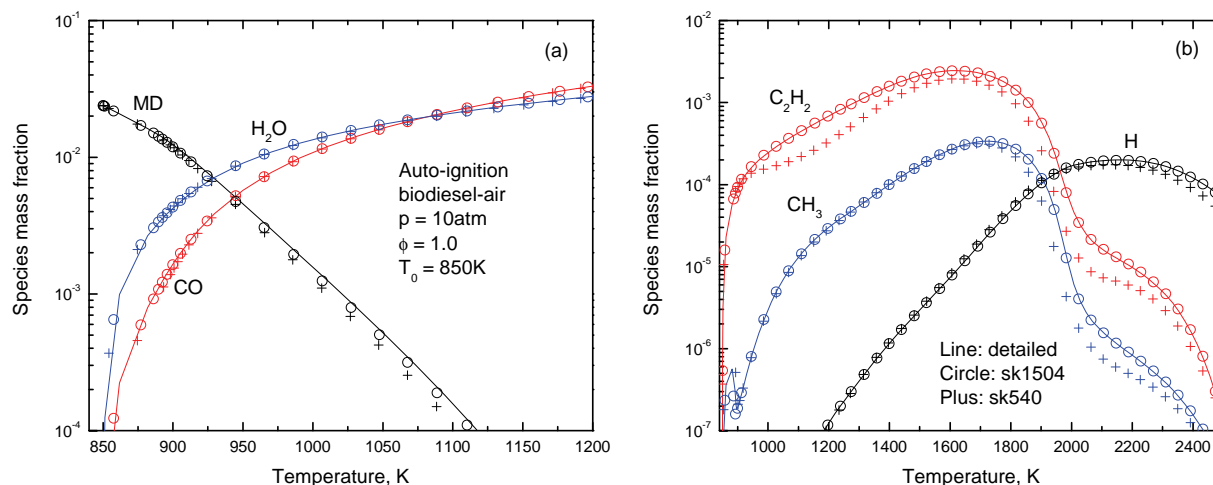


Figure 6. Comparison of species concentrations calculated using the detailed and skeletal mechanisms for auto-ignition of stoichiometric biodiesel-air at pressure of 10atm and initial temperature of 850K. a) major species, and b) intermediate species.

4. Concluding Remarks

The method of DRG is extended to allow expert-specified species-specific error tolerances for the species of interest. The DRGX method is more suitable than DRG to derive skeletal mechanism with high chemical fidelity from detailed mechanisms that consists of disparate uncertainties in reaction pathways. The DRGX methods reduces to DRG in the limit of small threshold error, ϵ , and large x-values. If x-values for too many species are specified, the DRGX method reduces to the manual selection of the species in the skeletal mechanism. Between the two limits the DRGX method can be employed to obtain skeletal mechanisms with balanced size and chemical fidelity. For practical simulations where the prediction of heat release rate is of the primary interest, DRGX with a small x_Q value can be performed in a similar way to the development of the present 540 species skeletal mechanism. While in studies where it is important to retain high fidelity of selected species, DRGX with larger sets of x-values can be adopted. In the present study, it was found that DRGX with post-processing of the x-values is adequate to achieve reasonably good accuracy, while if needed the more conservative DRGX/pre-processing approach can be chosen. The skeletal mechanisms derived using DRGX

can be further reduced through other approaches, similarly to those derived with DRG, based on the needs in specific studies.

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