Reduced chemistry for a gasoline surrogate valid at engine-relevant conditions

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Abstract

A detailed mechanism for the four-component gasoline surrogate developed by Lawrence Livermore National Laboratory has shown good agreement with experiments in engine-relevant conditions. However, with 1388 species and 5933 reversible reactions, this detailed mechanism is far too large to use in practical engine simulations. Therefore, reduction of the detailed mechanism was performed using a multi-stage approach consisting of the DRGEPSA method, unimportant reaction elimination, isomer lumping, and analytic QSS reduction based on CSP analysis. A new greedy sensitivity analysis algorithm was developed and demonstrated to be capable of removing more species for the same error limit compared to the conventional sensitivity analysis used in DRG-based skeletal reduction methods. Using this new greedy algorithm, several skeletal and reduced mechanisms were developed at varying levels of complexity and for different target condition ranges. The final skeletal and reduced mechanisms consisted of 213 and 148 species, respectively, for a lean, low-temperature HCCI-like range of conditions. For a lean-to-rich, high-temperature, SI/CI-like range of conditions, skeletal and reduced mechanisms were developed with 97 and 79 species, respectively. The skeletal and reduced mechanisms in this study were produced using an error limit of 10% and validated using homogeneous autoignition simulations over engine-relevant conditions—all showed good agreement in predicting ignition delay. Furthermore, extended validation was performed, including comparison of autoignition temperature profiles, PSR temperature response curves and extinction turning points, and laminar flame speed calculations.
Introduction

Modeling the kinetics of gasoline—as well as other liquid transportation fuels—is complex due to the near-continuous spectrum of constituent hydrocarbons. One widely used solution in the combustion community is to use surrogate fuels that consist of a small number of hydrocarbons representing the major hydrocarbon classes present in real gasoline. Historically, binary blends of \textit{n}-heptane and isooctane were used to model gasoline at various octane numbers; these are the primary reference fuels (PRFs)\textsuperscript{1–3}. However, in general these simple mixtures cannot match some key properties of gasoline. For example, the H/C ratio of gasoline is usually less than two\textsuperscript{4}, but PRFs are limited to the range of 2.3–2.25. In addition, PRFs cannot capture the so-called gasoline sensitivity, the difference between motor octane number (MON) and research octane number (RON); RON and MON are equal for any PRF mixture.

In order to better match the physical and kinetic properties of gasoline, a number of research groups developed surrogate formulations containing additional components used to represent other major hydrocarbon classes (e.g., olefins, aromatics). Gauthier et al\textsuperscript{5} and Chaos et al\textsuperscript{4} proposed three-component surrogates, adding toluene to \textit{n}-heptane and isooctane to form toluene reference fuels (TRFs). Recently, Mehl et al\textsuperscript{6,7} proposed a four-component gasoline surrogate consisting of \textit{n}-heptane, isooctane, toluene, and 2-pentene to represent linear alkanes, branched alkanes, aromatics, and olefins, respectively. They found that this surrogate emulates engine data, laminar flame speeds, and shock tube ignition delay times of the target gasoline with good agreement. Kukkadapu et al\textsuperscript{8,9} performed further experimental and computational validation of the surrogate mixture and representative kinetic mechanism of Mehl et al\textsuperscript{6}. They found that for stoichiometric mixtures the surrogate matched the autoignition response of the target gasoline in a rapid compression machine, and the mechanism predicted overall ignition delays of real gasoline with good agreement.

While the performance of the proposed gasoline surrogate mechanism is promising, the large size of the reaction mechanism—1388 species and 5933 reversible reactions—poses a significant challenge to practical engine simulations. The computational cost of chemistry scales by the third power of the number of species in the worst case\textsuperscript{10}. In three-dimensional, high-fidelity simulations of engines or combustion chambers where mesh sizes could range $10^4$–$10^7$ cells, chemistry calculations must be performed at least once for each grid point or cell. Therefore, significant reduction in mechanism size while retaining its predictive capabilities is vital in order to use the mechanism in practical simulations. The objective of this study is to (1) develop and demonstrate a multi-stage mechanism reduction methodology capable of achieving the above task, and (2) produce compact skeletal and reduced mechanisms for the aforementioned gasoline surrogate capable of predicting key phenomena.

A number of mechanism reduction methods have been developed in recent years to counter the trend of increasing mechanism sizes, as reviewed by Lu and Law\textsuperscript{10}. Most approaches focus on identifying and removing unimportant species, or performing “skeletal” reduction. Many methods have been developed, but one class that received significant development is based on the directed relation graph (DRG)\textsuperscript{11–13}. Similar to the earlier graphical representation of reaction pathways of Bendtsen et al\textsuperscript{14}, DRG quantifies the importance of species using normalized contributions to the overall production rates of certain (preselected) important target species. Since the introduction of DRG, a number of variants have been developed, including DRG-aided sensitivity analysis (DRGASA)\textsuperscript{15,17}, DRG with error propagation (DRGEP)\textsuperscript{18,19}, DRGEP with sensitivity analysis (DRGEP-SA)\textsuperscript{20,21}, and path-flux analysis\textsuperscript{22}. 

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Another reduction paradigm focuses on time-scale analysis, identifying and removing short timescales—induced by rapidly depleting species and/or fast reversible reactions—that cause chemical stiffness. Many methods rely on the classical quasi-steady state (QSS) and partial equilibrium approximations, which replace differential equations with algebraic relations for some species. Originally, such species and reactions were identified on the basis of experience and intuition, but systematic methods that use analysis of the Jacobian matrix to identify QSS species and partial equilibrium reactions, namely the computational singular perturbation (CSP) and intrinsic low-dimensional manifold methods, have since been developed.

Finding a single skeletal reduction stage not sufficient to reduce the size of large detailed mechanisms, Lu and Law presented a multi-stage reduction strategy and applied it to a detailed mechanism for n-heptane. Their approach consisted of DRGASA, unimportant reaction elimination, isomer lumping, and time scale reduction through the QSS approximation. In addition, they grouped similar diffusive species in the final reduced mechanism to reduce the cost of the mixture-averaged diffusion formulation.

In this work, we apply a multi-stage reduction strategy similar to that developed by Lu and Law based on DRGEPSA to the large detailed mechanism for gasoline surrogates of Mehl et al. We selected DRGEPSA for the base skeletal reduction method following the demonstration of Niemeyer et al. that DRGEPSA can produce more compact skeletal mechanisms for the same level of accuracy than DRG, DRGEP, and DRGASA. In the first stage, the DRGEPSA method is applied to remove a large number of unimportant species (and corresponding reactions). Second, a stage of further unimportant reaction elimination is performed to remove additional reactions; this step does not affect the number of species, but the complexity of the mechanism is reduced. Third, a final skeletal mechanism is produced after identifying and lumping isomers. Finally, QSS species are identified using CSP analysis and an analytic solution for the QSS species concentrations is generated. We then validate the resulting skeletal and reduced mechanisms over engine-relevant conditions, comparing the performance against that of the detailed mechanism in predicting global phenomena such as homogeneous, adiabatic ignition delays, perfectly stirred reactor extinction turning points, and laminar flame speeds; in addition, comparisons between local temperature evolution profiles in autoignition provide more rigorous validation.

In the following sections, we will first describe the above multi-stage reduction methodology. A new greedy sensitivity analysis algorithm will be introduced and developed that can achieve greater reduction than the conventional algorithm for the same error limit. Then, skeletal and reduced mechanisms at varying levels of complexity will be generated using our reduction approach. Finally, validation of the skeletal and reduced mechanisms will be performed, followed by a discussion of these results.

**Methodologies**

In the current work, we applied a multi-stage reduction procedure that consisted of a number of previously developed techniques—although most were updated and improved—to the detailed mechanism for gasoline surrogates of Mehl et al. The mechanism, developed to represent a four-component surrogate of gasoline (isoctane, n-heptane, toluene, and 2-pentene), consists of 1388 species and 5933 reversible reactions. As discussed by Niemeyer and Sung previously, the current version of this mechanism contains a dead-end pathway terminating with the nC₄H₃
radical; as such, this species and the two reactions in which it participates were removed prior to mechanism reduction and later validation. The gasoline surrogate formulation consists of 48.8% isooctane, 15.3% \textit{n}-heptane, 30.6% toluene, and 5.3% 2-pentene (by molar percentage), denoted as the LLNL surrogate hereafter.

Two different ranges of conditions were used: one targeted at low-temperature homogenous charge compression ignition (HCCI) engine conditions, and the second targeted at more traditional spark- or compression-ignition (SI/CI) engine conditions at higher temperatures. Thermochemical data for the HCCI-like conditions were generated using constant-volume autoignition simulations performed using the initial conditions listed in Table 1, based on a similar set used by Mehl et al. These include a range of conditions covering initial pressures of 10–60 atm, temperatures of 750–1200 K, and equivalence ratios of 0.2–1.0.

For the SI/CI engine conditions, we used autoignition initial conditions covering 1000–1400 K, 1–40 atm, and equivalence ratios of 0.5–1.5. In addition, since the target phenomena include high-temperature flame propagation, for this range of conditions we performed the reduction including perfectly stirred reactor (PSR) data—in addition to that from autoignition—covering the same range of pressure and equivalence ratios with an inlet temperature of 300 K.

Autoignition data were sampled densely during the ignition evolution, as described previously. PSR data were sampled at three points along the upper stable branch of the temperature response curve: (1) at the extinction turning point, (2) the point closest to 0.1 s, and (3) the logarithmic midpoint between points one and two. For both reductions, we applied an error limit of 10%, corresponding to error in ignition delay for the autoignition simulations. For the PSR simulations, the error corresponded to the maximum error in predictions of the extinction turning point (point one) residence time and the temperature at points two and three. For both sets of conditions, we selected isooctane, \textit{n}-heptane, toluene, 2-pentene, oxygen, and nitrogen (to prevent removal) as the DRGEP target species.

Both the autoignition and PSR simulations were parallelized using OpenMP, such that multiple simulations may be performed simultaneously. This greatly reduced the runtime of the original sampling of the detailed mechanism in addition to that of the overall reduction process.

**Reduction procedure**

**Skeletal reduction stages**

First, we applied the DRGEPSA method, as described by Niemeyer et al., to remove a large number of species and reactions from the detailed mechanism. We describe this method briefly here; further detail can be found in our prior work. The DRGEPSA method consists of first to quantify the importance of species to predetermined target species through a graph-based representation of species interdependence in the reaction system. After forming the graph by quantifying the interdependence of all species pairs, a graph search is performed using Dijkstra’s algorithm, initiating at the user-determined target species. Species are then declared unimportant and removed when their importance value (overall importance coefficient, $R_{AB}$) falls below a cutoff threshold $\varepsilon_{EP}$, which is determined iteratively based on the user-specified error limit. Following the application of DRGEP, sensitivity analysis (SA) is performed on certain remaining

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1 The logarithmic midpoint, or geometric mean, is equal to the square root of the product of the surrounding points, i.e., $x_2 = \sqrt{x_1 \times x_3}$. 

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“limbo” species based on their $R_{AB}$ values. Species with overall importance coefficients above an upper threshold value ($\varepsilon^*$) are automatically retained, while the limbo species, for which $\varepsilon_{EP} \leq R_{AB} < \varepsilon^*$, are considered individually for removal.

Previously used sensitivity analysis approaches removed limbo species one-by-one, arranged them in ascending order based on the error induced to the mechanism by their removal, and then removed the limbo species in this order until the global error reached a limit. We refer to this approach in the following as the “initially informed” sensitivity analysis algorithm. Here, we introduce an improved sensitivity analysis algorithm based on a novel “greedy” approach. Greedy algorithms make locally optimal decisions with the goal of reaching global optima, using current information to make the choice that appears best. The new greedy sensitivity analysis algorithm first evaluates the error induced by the removal of each species, given by

$$\delta_S = |\delta_{S,\text{ind}} - \delta_{\text{skel}}| ,$$

(1)

where $\delta_{\text{skel}}$ is the error of the current skeletal mechanism (prior to temporary removal of limbo species $S$) and $\delta_{S,\text{ind}}$ the error induced by the removal of limbo species $S$, by removing each one-by-one. Then, using the criterion given by Eq. (Eq. (1)), the algorithm identifies the limbo species with the smallest induced error and removes it; this procedure is repeated until the maximum error reaches the user-specified limit. By using $\delta_S$ rather than $\delta_{S,\text{ind}}$, the species whose removal affects the mechanism the least is selected for removal. Admittedly, this sensitivity analysis algorithm is computationally expensive due to the large number of error evaluations (and associated autoignition/PSR simulations), but it is made more tractable by the DRGEP stage initially eliminating a large number of species from the starting detailed mechanism.

In contrast, the previous initially informed sensitivity analysis algorithm used only the species’ original induced error information. In that case, following the initial species removal the ordering of species is based on outdated information, leading to potentially suboptimal decisions for removal. Therefore, the algorithm could exit early, resulting in a larger-than-necessary skeletal mechanism. We will compare the results of the original initially informed and new greedy sensitivity analysis algorithms in due course.

Following the application of DRGEP$\text{SA}$, an additional step of further unimportant reaction elimination was performed based on the methodology of Lu and Law. This method uses the CSP importance index to quantify the importance of reactions to all species in the mechanism. As with the DRGEP method, the cutoff threshold for reaction importance was determined iteratively based on error limit.

Next, we applied an isomer lumping stage to further reduce the number of species. Due to the similarity of many isomers’ thermodynamic and transport properties, such species can be lumped together in the chemical kinetics and transport equations. While more complex lumping strategies exist, our procedure—following that of Lu and Law—is based on the observation that many isomers mass fractions are correlated to the mass fraction of their group (the sum of the isomers that comprise the group):

$$Y_{k,j} = \alpha_{k,j} Y_j ,$$

(2)

where $Y_{k,j}$ represents the mass fraction of isomer $k$ in group $j$, $Y_j$ is the mass fraction of isomer group $j$, and $\alpha_{k,j}$ is a constant coefficient. For each group of isomers we determined the constant $\alpha_{k,j}$ by sampling the isomer mass fractions using autoignition/PSR simulations and performing a
linear regression. To ensure the validity of data points, we only used reaction states where the isomer group mass fraction was non-negligible (i.e., where \( Y_j \geq 10^{-10} \)). In addition, we only selected isomers for lumping when the coefficient of determination (i.e., \( r^2 \) value) was above a certain threshold, determined iteratively based on error. Once the isomer coefficients were determined, the skeletal mechanism was lumped by replacing each isomer with a notional species for the group, and modifying the Arrhenius coefficients of reactions where the isomer is a reactant with the coefficient \( \alpha_{k,j} \).

**Time-scale reduction stage**

The final reduction stage involved applying the QSS approximation to species identified using the CSP analysis of Lam and coworker\(^{27-29,36}\), and follows a similar approach to that of Lu and Law\(^{17,37}\). The reaction system can be represented with the ODEs

\[
\frac{dy}{dt} = g(y), \quad \text{and} \\
\frac{dg}{dt} = Jg, \quad J \equiv \frac{dg}{dy},
\]

where \( y \) is the species concentration vector, \( g \) is the species production rate vector, and \( J \) is the Jacobian matrix. CSP analysis decomposes the source terms \( g \) into “modes” using basis vectors:

\[
f = Bg, \\
\frac{df}{dt} = \Lambda f, \\
\Lambda = \left( \frac{dB}{dt} + BJ \right) A, \\
A = B^{-1},
\]

where the matrices \( A \) and \( B \) hold the column and row basis vectors, respectively, and \( f \) is the vector of modes. Practically, this procedure is implemented by calculating the Jacobian \( J \) using a sixth-order central finite difference, then using the LAPACK subroutine DGEEV\(^{38}\) to calculate the eigenvalues and eigenvectors. The Jacobian is assumed to be time independent such that the basis rotation term \( \frac{dB}{dt} = 0 \), and as a result Eq. (7) becomes

\[
\Lambda = BJA, \\
\]

or

\[
J = A\Lambda B,
\]

where the diagonal elements of \( \Lambda \) are the eigenvalues of \( J \), the columns of \( A \) contain the right eigenvectors, and the rows of \( B \) contain the left eigenvectors.

Next, the fast and slow subspaces are separated, such that

\[
\frac{d}{dt} \begin{pmatrix} f_{\text{fast}} \\ f_{\text{slow}} \end{pmatrix} = \begin{pmatrix} \Lambda_{\text{fast}} & \Lambda_{\text{slow}} \end{pmatrix} \begin{pmatrix} f_{\text{fast}} \\ f_{\text{slow}} \end{pmatrix}.
\]
The fast modes are those that rapidly exhaust and decay, while the slow modes remain important and control the overall behavior of the system. The eigenvalues associated with fast modes—the diagonal elements of $\Lambda_{\text{fast}}$—are negative with a much larger magnitude than the eigenvalues associated with the slow modes, contained in $\Lambda_{\text{slow}}$. The separation of the fast and slow subspaces is identified by a timescale analysis:

$$
\frac{-1}{\lambda_{\text{min}}(\Lambda_{\text{fast}})} \equiv \tau_{\text{fast}} < \frac{\tau_c}{\alpha_{\text{CSP}}},
$$

(12)

where the time scale of the fast subspace ($\tau_{\text{fast}}$) is the negative inverse of the smallest magnitude eigenvalue ($\lambda_{\text{min}}$) in $\Lambda_{\text{fast}}$, $\tau_c$ is a characteristic time scale of the reacting system (e.g., autoignition delay, extinction turning point residence time), and $\alpha_{\text{CSP}}$ is a safety factor (e.g., 100).

Once the fast and slow subspaces are separated, the species rates of production can be projected onto the two subspaces:

$$
g = \left( Q_{\text{fast}} + Q_{\text{slow}} \right) g,
$$

(13)

where the fast and slow projection matrices are

$$
Q_{\text{fast}} = A_{\text{fast}} B_{\text{fast}}, \quad \text{and}
$$

(14)

$$
Q_{\text{slow}} = A_{\text{slow}} B_{\text{slow}},
$$

(15)

respectively. The $i$th species is considered QSS if it satisfies the following condition over the entire parameter range of interest:

$$
\left| Q_{\text{slow},i,i} \right| < \varepsilon_{\text{CSP}},
$$

(16)

where $Q_{\text{slow},i,i}$ is the $i$th diagonal element of $Q_{\text{slow}}$ and $\varepsilon_{\text{CSP}}$ is a small threshold value.

Once the set of QSS species are selected, applying the QSS approximation results in a set of nonlinear algebraic equations for the concentrations of each species, coupled with the remaining differential equations governing the non-QSS species. Past efforts focused on solving this system of equations through iterative schemes, but convergence difficulties can arise due to deterioration of the QSS assumption when near and outside the validity range, leading to excessive computational cost. An alternative is to linearize the relations—assuming the coupling between QSS species is sparse in general—and generate an analytical solution for the concentrations of the QSS species. Here, we present such a methodology, adopted from the approach established by Lu and Law, who also presented greater detail and explanation of this method. We summarize the necessary steps here.

First, we must ensure the contribution of the nonlinear terms in the QSS equations is negligible such that these terms can be eliminated from the relations. According to the QSS approximation, the net production rate of a QSS species is small compared to both the production and consumption rates. This approximation results in a system of algebraic equations for the QSS species:

$$
\omega_{p,i} = \omega_{C,i} \quad i = 1,2,\ldots,N,
$$

(17)
with the species production and consumption rates expressed as

$$\omega_{P,i} = \sum_{j=1}^{N_R} v_{i,j}' \Omega_j$$ \quad and \quad $$\omega_{C,i} = \sum_{j=1}^{N_R} v_{i,j}' \Omega_j,$$ \quad (18)

respectively, where \(N\) is the number of QSS species and \(N_R\) the number of irreversible reactions. Note that unlike the previous reduction stages, this step requires all reactions to be irreversible. The reaction rate is calculated using

$$\Omega_j = k_j \prod_{k=1}^{N_S} x_k,$$ \quad (19)

where \(k_j\) is the Arrhenius rate coefficient, \(N_S\) the total number of species (both QSS and non-QSS), and \(x_k\) the molar concentration of the \(k\)th species. Equation (Eq. (17)) may be nonlinear due to the participation of multiple QSS species or a stoichiometric coefficient greater than one for a particular QSS species in a reaction. However, due to the typically low concentration of QSS species (after an initial transient period), these nonlinear terms may not be important. This importance can be quantified by calculating the normalized contribution of the nonlinear terms to the production and consumption rates of the \(i\)th QSS species, expressed as

$$\pi_i = \sum_{j=1}^{N_R} v_{i,j}' \Omega_j \delta_j / \omega_{P,i},$$ \quad and \quad

$$\kappa_i = \sum_{j=1}^{N_R} v_{i,j}' \Omega_j \delta_j / \omega_{C,i},$$ \quad (20, 21)

respectively, where

$$\delta_j = \begin{cases} 1 & \text{if reaction } j \text{ involves } > 1 \text{ QSS reactant,} \\ 0 & \text{otherwise}. \end{cases}$$ \quad (22)

These measures of importance are similar to those used in DRG/DRGEP as well as unimportant reaction elimination, and here—as in those methods—the terms are considered unimportant if the values fall below a cutoff threshold. The nonlinear terms may be neglected if

$$\max_{k \in \{\mathcal{S}\}} \left( \max_{\text{all QSS species } i,k} \pi_i \right) < \varepsilon_{\text{nonlin}}$$ \quad and \quad (23)

$$\max_{k \in \{\mathcal{S}\}} \left( \max_{\text{all QSS species } i,k} \kappa_i \right) < \varepsilon_{\text{nonlin}},$$ \quad (24)

where \(k\) is a reaction state, \(\{\mathcal{S}\}\) the set of all reaction states of interest, and \(\varepsilon_{\text{nonlin}}\) a small user-defined threshold (e.g., 0.1–0.2). The nonlinear contributions to QSS equations are deemed negligible and removed if Eqs. (Eq. (23)) and (Eq. (24)) is satisfied.

Once the nonlinear terms are eliminated, the QSS relations in Eq. (Eq. (17)) can be expressed using a system of linear equations, which Lu and Law\textsuperscript{40} termed the linearized QSS approximation
(LQSSA):

\[ C_i x_i = \sum_{k \neq i} P_{ik} x_k + P_{i0} \quad i = 1, 2, \ldots, N, \] \hspace{1cm} (25)

where

\[ C_i = \frac{\omega_{C,i}}{x_i}, \] \hspace{1cm} (26)

\[ P_{ik} = \frac{\sum_{j=1}^{N_R} v_{i,j}'' \Omega_j \text{sgn} \left( v_{k,j}' \right)}{x_k}, \] \hspace{1cm} (27)

\[ P_{i0} = \sum_{j=1}^{N_R} v_{i,j}'' \Omega_j \delta_j', \] \hspace{1cm} (28)

\[ \text{sgn} \left( v_{k,j}' \right) = \begin{cases} 1 & \text{if } v_{k,j}' > 0, \\ 0 & \text{if } v_{k,j}' = 0, \end{cases} \] \hspace{1cm} (29)

\[ \delta_j' = \begin{cases} 1 & \text{if reaction } j \text{ involves no QSS species as reactant,} \\ 0 & \text{otherwise.} \end{cases} \] \hspace{1cm} (30)

Note that the consumption and production coefficients \( C_i, P_{ik}, \) and \( P_{i0} \) are independent of QSS species concentrations, and are either positive or zero.\(^2\) As with the initial nonlinear QSS relations, the system of equations given by Eq. (Eq. (25)) may be solved by iterative schemes, but could suffer the same computational difficulties. In addition, the system could be solved through the typical Gaussian elimination, but its algorithmic complexity is a cubic function of \( N \). Instead, an analytic solution based on variable substitution and elimination offers an efficient approach for calculation the QSS species concentrations. Now, the challenge becomes finding the best order for elimination by substitution that minimizes the number of operations required. Lu and Law\(^{40} \) proposed using graph theory to identify the interdependence of QSS species. We detail the construction of such a QSS graph (QSSG) in the following section.

The system of LQSSA equations, as given by Eq. (Eq. (25)), can be transformed to a form that offers a direct solution for each variable:

\[ x_i = \sum_{k \neq i} A_{ik} x_k + A_{i0} \quad i = 1, 2, \ldots, N, \] \hspace{1cm} (31)

where

\[ A_{ik} = \frac{P_{ik}}{C_i} \quad \text{and} \quad A_{i0} = \frac{P_{i0}}{C_i}. \] \hspace{1cm} (32)

In this formulation, the solution for the concentration \( x_i \) directly requires \( x_k \) if \( A_{ik} > 0 \). Similar to the concept used in DRG/DRGEP, the dependence of QSS species concentrations on one another can be mapped to a directed graph, where each QSS species is a graph node. Edges between nodes exist when there is a direct dependence between species: the edge \( x_i \to x_k \) exists if and only if \( A_{ik} > 0 \). In some cases, Eq. (Eq. (31)) may be explicit for all QSS species—meaning there is no interdependence—and the equations can be solved in order without the need to substitute

\(^2\)Although the QSS species concentrations \( x_i \) and \( x_k \) appear in the denominators of Eqs. (Eq. (26)) and (Eq. (27)), they are already present in the numerators through \( \omega_{C,i} \) and \( \Omega_j \) and therefore cancelled out.
expressions and eliminate variables. In general, though, the QSSG will consist of strongly coupled
groups of species that form cycles of dependence—these are known as the strongly connected
components (SCCs) of the graph. Intergroup coupling, on the other hand, is acyclic, such that an
explicit solution order of groups may be determined.

One important step is to prune the QSSG of unimportant edges, again in a similar manner to
the elimination of unimportant species in the DRG and DRGEP methods. While less important
when a small number of QSS species exist, trimming the edges in a large graph ensures that the
matrix $A$ formed by the coefficients $A_{ik}$ is sparse, resulting in multiple groups rather than one large
cyclic group made up of all the QSS species. The importance of QSSG edges can be determined
by calculating the normalized contribution of the $k$th QSS species to the production rate of the $i$th
QSS species:

$$
\frac{r_{ik}}{\max_{\mathcal{D}} \left( \frac{A_{ik}x_k}{\sum_{j \neq i} A_{ij}x_j + A_{i0}} \right)},
$$

where $\max_{\mathcal{D}}$ indicates taking the maximum value over the set of all reaction states of interest
$\mathcal{D}$. Unimportant QSSG edges are then identified and removed through comparison with a small
cutoff threshold $\varepsilon_{QSS}$, such that the remaining edges satisfy

$$
x_i \rightarrow x_k \iff r_{ik} \geq \varepsilon_{QSS}.
$$

After pruning the graph edges, the next step is to identify the SCCs and perform a topological sort,
which provides the order in which the SCCs are to be solved. This is performed using the
DIGRAPH_ADJ_COMPONENTS subroutine of Burkardt’s GRAFPACK, with the algorithm
originally taken from Thulasiraman and Swamy. The adjacency matrix $E$ of the QSSG, a neces-
sary input, is formed by

$$
E_{ik} = \begin{cases} 1, & \text{if there is an edge } x_i \rightarrow x_k, \\ 0, & \text{otherwise.} \end{cases}
$$

With the SCCs identified and sorted, the only remaining task is to solve for the intra-SCC species
concentrations through variable elimination by substitution. Lu and Law proposed a method to
identify a near-optimal sequence for variable elimination, by calculating the normalized expansion
cost $c_i$ of each variable $x_i$, defined as

$$
c = Lc,
$$

where

$$
E_{ik} = \frac{A_{ik}x_k}{\sum_{j=1}^{M} E_{jk}},
$$

and $M$ is the number of QSS species in the current SCC. Equation (Eq. (36)) is an eigenvalue prob-
lem, where the column vector $c$ is the eigenvector of $L$ associated with the principal eigenvalue. We
solved this equation using the LAPACK subroutine DGEEV and selected the resulting eigen-
vector associated with the largest eigenvalue. The values of $c$ represent the relative expansion cost
of each QSS species in the SCC, such that species with lower $c_i$ values should be eliminated from
later expressions first. Therefore, species within the SCC are sorted in ascending order of $c_i$ for elimination by substitution.

Finally, we note that in some cases, the LQSSA—and therefore the analytic QSS solution—may not be valid when the contributions from the nonlinear terms ($\pi_i$ and $\kappa_i$) are not negligible. For example, Lu and Law\textsuperscript{40} compared the terms’ importance to detailed and skeletal mechanisms for ethylene, consisting of 70 and 33 species, respectively. They found that while the terms were in fact small (between 0.1–0.2) for the skeletal mechanism, the same was not true for the detailed mechanism, where the nonlinear contributions to the production rates ($\pi_i$) were nearly unity in some cases. It remains to be seen whether the LQSSA approximation is valid in the case of larger, more complex skeletal mechanisms resulting from even larger initial detailed mechanisms.

When non-negligible nonlinear terms exist in the skeletal mechanism, two main options exist: (1) remove offending species from the QSS list, such that the nonlinear terms become negligible; and (2) develop a hybrid analytic-iterative solution scheme, where most of variables are calculated analytically and a small number of nonlinear terms are solved iteratively. In the current study, no selected values of $\varepsilon_{CSP}$ resulted such in a situation, so we did not need to pursue either option.

**Reduction package**

The updated DRGEPSA method, the unimportant reaction elimination stage, the new isomer lumping stage, and the analytic QSS reduction stage were incorporated into the latest version of the Mechanism Automatic Reduction Software (MARS) package\textsuperscript{20,21,31}. This software is available by request to the authors.

A skeletal mechanism is generated as a collection of elementary reactions in the standard CHEMKIN format\textsuperscript{43}, which may be easily used with any chemical kinetics platform. In contrast, a reduced mechanism requires a custom subroutine for evaluating the non-QSS species production rates along with the QSS species concentrations. More implementation details involving reduced mechanisms may be found in, e.g., Chen\textsuperscript{44} or Sung et al.\textsuperscript{45,46}

**Results and Discussion**

**Mechanism reduction**

**HCCI-like conditions**

First, we compared the performance of the initially informed and greedy sensitivity analysis algorithms in DRGEPSA. For the HCCI-like set of conditions, these algorithms resulted in skeletal mechanisms with 344 species and 1645 reactions, and 233 species and 1061 reactions, respectively, with maximum errors of 9.3% and 8.9% (based on the set of initial conditions given in Table 1). In addition, we validated the ignition delay predictions of both skeletal mechanisms over the full target range of conditions; both mechanisms performed well, as shown in Figure 1 using $\phi = 0.5$ for the LLNL gasoline surrogate in air. The greater extent of reduction of the greedy sensitivity analysis—removing nearly 100 species more than the initially informed algorithm—while retaining a similar level of performance suggest the usefulness of the algorithm.

Using the greedy SA-generated mechanism for the remaining analysis, the results from all reduction stages are summarized in Table 2. For DRGEPSA, the cutoff threshold and upper threshold
for sensitivity analysis were \(7 \times 10^{-3}\) and 0.1, respectively. The unimportant reaction elimination algorithm selected a cutoff threshold for reactions of \(6 \times 10^{-3}\). Out of 40 potential isomer groups containing a total of 125 species, only seven groups with 27 isomers were selected using an error-based coefficient of determination cutoff of 0.995. The isomers and their groups are listed in Table 3. The small number of isomers selected for lumping suggested that isomer mass fractions are less correlated at the lower temperatures experienced in this range of conditions; Luo et al. \(^{47}\) experienced similar behavior when generating a skeletal mechanism for biodiesel surrogates valid at low temperatures. For the CSP-based QSS reduction stage, we selected \(\alpha_{\text{CSP}} = 100\) and \(\epsilon_{\text{CSP}} = 1 \times 10^{-4}\), using the QSSG cutoff threshold \(\epsilon_{\text{QSS}} = 0.01\).

We note that the QSS reduction parameters (\(\alpha_{\text{CSP}}, \epsilon_{\text{CSP}}, \text{and } \epsilon_{\text{QSS}}\)) were chosen based on trial and error. Lu and Law \(^{17,37}\) used “jumps” in the numbers of QSS species as a function of \(\epsilon_{\text{CSP}}\) to select the best values for methane and \(n\)-heptane reduced mechanisms, choosing 0.1 in both cases. Figure 2a shows this relationship for the current situation plotted in a linear format, for the skeletal mechanism following isomer lumping with 213 species and 910 reactions. Similar jumps in number are observed—in fact, Figure 2a appears nearly identical to those shown by Lu and Law \(^{17,37}\)—but we found that more care must be taken in selecting \(\epsilon_{\text{CSP}}\). For example, by taking the value 0.15 based on the first major jump in Figure 2a, we produced a reduced mechanism with 82 non-QSS and 131 QSS species. This mechanism performed poorly, demonstrating a maximum error of 825.6%. In addition, the maximum contribution of the (removed) nonlinear QSS terms \(\pi_i\) and \(\kappa_i\) were both non-negligible, around 0.6. Practically, the large number of QSS species resulted in an incredibly complex analytic solution for the QSS species concentrations, producing a Fortran source code file with over 60,000 lines.

Obviously, \(\epsilon_{\text{CSP}} = 0.15\) was too large for this case. In order to select a more appropriate value, we replotted the relationship between \(\epsilon_{\text{CSP}}\) and number of QSS species into a semilogarithmic format, as shown in Figure 2b. Viewed in this manner, a number of jumps were observed. We selected \(1 \times 10^{-4}\) based on the location of one jump (as well as trial-and-error), and this resulted in a reduced mechanism with 148 non-QSS and 65 QSS species that performed within the 10% error limit; additionally, the nonlinear contributions remained negligible (< \(5 \times 10^{-6}\)). A more systematic approach to determining the optimal \(\epsilon_{\text{CSP}}\) values is warranted, which will be pursued in future work. For example, one option may be to select \(\epsilon_{\text{CSP}}\) based on the values of the contribution of nonlinear terms.

Finally, the parameter \(\epsilon_{\text{QSS}}\) was chosen as 0.01 in order to simplify the QSS analytic solution without introducing significant error. Using \(\epsilon_{\text{QSS}} = 0\) (i.e., retaining the entire QSSG) produced a reduced mechanism that performed with a maximum error of 9.3%. However, this resulted in a Fortran source code file unable to be compiled by some compilers due to long expressions: the longest expression required over 1300 lines with about 200 characters per line. Raising \(\epsilon_{\text{QSS}}\) to 0.01 simplified the system considerably, such that the longest expression only needed 13 lines, while negligibly increasing error.

**SI/CI conditions**

As in the previous section, we first compared the results of the initially informed and greedy sensitivity analysis algorithms in order to further investigate the new algorithm. Using both autoignition and PSR simulation data with \(\epsilon^* = 0.5\), the initially informed algorithm generated a skeletal mechanism with 330 species and 1951 reactions, with a maximum error of 8.4%. In contrast, the
greedy algorithm gave a mechanism with 98 species and 611 reactions, predicting ignition delay with a maximum error of 9.1% over the set of initial conditions. Figure 3 shows the ignition delay predictions of the skeletal mechanisms produced by the initially informed and greedy algorithms for a range of initial temperatures and pressures at $\phi = 1.0$; both reproduced the calculations of the detailed mechanism at all conditions nearly identically, although clearly the greedy algorithm produced a notably smaller skeletal mechanism.

In order to study the effects of varying $\varepsilon^*$ and using PSR in the reduction procedure on the two sensitivity analysis algorithms, we also generated additional skeletal mechanisms using different combinations of parameters as summarized in Table 4. Interestingly, the low and high extremes in terms of resulting skeletal mechanism sizes resulted from the greedy and initially informed SA algorithms, respectively, using autoignition and PSR data with a relatively high $\varepsilon^*$ value. The greedy algorithm combined with a typical $\varepsilon^*$ value (e.g., 0.1) resulted in a skeletal mechanism that not only contained a larger number of species but also performed poorly outside of autoignition (e.g., PSR, laminar flame speed calculations); this occurred due to the overaggressive removal of species unimportant to autoignition but important in other phenomena. Niemeyer and Sung previously demonstrated this issue when reducing detailed mechanisms for multicomponent surrogates, and suggested decreasing $\varepsilon^*$ would prevent the removal of these species. Unfortunately, as shown here, the cost of this solution is a larger resulting mechanism size. Interestingly, with $\varepsilon^* = 0.01$ both algorithms produced similarly sized skeletal mechanisms; due to the severe limitations on the number of limbo species, the improved greedy algorithm was not able to perform more effectively. Overall, our results suggest that using the greedy SA algorithm combined with PSR data (in addition to the default autoignition) and a high $\varepsilon^*$ value is the best approach in terms of both the size and performance of the resulting skeletal mechanism. Therefore, the skeletal mechanism associated with that approach is used for the following results and discussion.

Table 5 summarizes the results of each reduction stage. The DRGEP algorithm selected a cutoff threshold of $3 \times 10^{-3}$, and as mentioned above we set $\varepsilon^* = 0.5$ for the (greedy) sensitivity analysis upper threshold. The unimportant reaction elimination algorithm selected a cutoff threshold for reactions of $4 \times 10^{-3}$. Out of eight potential isomer groups containing a total of 21 species, the isomer lumping algorithm selected only one group with three isomers ($C_7H_{15}$-2, $C_7H_{15}$-3, and $C_7H_{15}$-4) using an automatically selected coefficient of determination cutoff of 0.994. For the CSP-based QSS reduction stage, based on the HCCI reduction results we selected $\alpha_{CSP} = 100$ and $\varepsilon_{CSP} = 1 \times 10^{-4}$, using the QSSG cutoff threshold $\varepsilon_{QSS} = 0.01$. Using these combinations of parameters, none of the QSS equations contained nonlinear terms and so no approximation was required here.

Regarding the CSP parameters, Figure 4 shows the relationship between the number of QSS species and the CSP cutoff threshold $\varepsilon_{CSP}$; the trends resemble those seen in Figure 2 for the HCCI-condition reduction, although even more dramatic jumps are observed (e.g., near $\varepsilon_{CSP} = 0.1, 0.4,$ and 0.8). In this case, selecting $\varepsilon_{CSP} = 0.1$ led to a reduced mechanism with 51 non-QSS and 46 QSS species that performed well in both the autoignition and PSR calculations considered; however, convergence problems arose during laminar flame speed calculations. Therefore, the lower value of $1 \times 10^{-4}$ was selected as described above, resulting in 79 non-QSS and 18 QSS species.
Mechanism validation

HCCI-like conditions

We performed validation of the skeletal and reduced mechanisms for the HCCI-like condition set using constant-volume autoignition simulations over a range of initial conditions for temperature, pressure, and equivalence ratio. Figure 5 shows the comparison of the ignition delays calculated by the detailed mechanism, skeletal mechanism resulting from the isomer lumping stage, and final reduced mechanism. Both the skeletal and reduced mechanisms performed well over the full range of conditions with the maximum error within 10%, despite some visible discrepancies at high temperatures and low temperatures/high pressures. Both mechanisms captured the negative temperature coefficient regimes for $\phi = 0.5$ and $1.0$.

Encouraged by the accurate prediction of ignition delay shown by the skeletal and reduced mechanisms, we also performed a more detailed validation analysis by comparing the temperature profiles for constant-volume autoignition initiating at different temperatures. As we showed previously\textsuperscript{21}, predicting the point of ignition does not guarantee prediction of time- or spatially-varying scalars. Figure 6, Figure 7, and Figure 8 show comparisons of temperature profiles for various initial temperatures at 10 atm and $\phi = 0.6$, 40 atm and $\phi = 1.0$, and 60 atm and $\phi = 0.2$, respectively. In general, both the skeletal and reduced mechanisms accurately reproduced the temperature profiles. Notably, the skeletal and reduced mechanisms performed indistinguishably.

Slight discrepancies in the point of ignition were observed as expected, and for certain conditions the skeletal and reduced mechanisms also underpredicted the post-ignition temperature slightly. Luo et al.\textsuperscript{47} observed similar errors for some conditions in their biodiesel skeletal mechanism produced using DRGASA with autoignition, PSR, and jet stirred reactor data; the source of these discrepancies is not clear. Comparing post-ignition temperatures calculated by skeletal mechanisms at varying stages in the reduction procedure, we traced this error back to the sensitivity analysis stage—the DRGEP-generated mechanism closely matched the detailed mechanism. Both the initially informed and greedy algorithms introduced this error. One potential cause may be the removal of species important to high-temperature heat release, but additional research in this direction is warranted. However, even with these errors in post-ignition temperature for some conditions, both the skeletal and reduced mechanisms captured the two-stage ignition seen at lower temperatures for all three pressure/equivalence ratio combinations.

SI/CI conditions

Next, we performed validation of the skeletal and reduced mechanisms for SI/CI conditions using constant-volume autoignition simulations over a range of initial conditions for temperature, pressure, and equivalence ratio. Figure 9 shows the comparison of the ignition delay times calculated by the detailed mechanism, skeletal mechanism resulting from the isomer lumping stage, and final reduced mechanism. Both the skeletal and reduced mechanisms performed well over the full range of conditions considered, identically reproducing the ignition delays calculated by the detailed mechanism.

In addition, we performed extended validation of the skeletal and reduced mechanisms using PSR and laminar flame speed simulations. Figure 10 shows the PSR temperature response curves for pressures of 1, 20, and 40 atm, equivalence ratios ranging over 0.5–1.5, and an inlet temperature of 300 K. Both the skeletal and reduced mechanisms reproduced the curves of the detailed mech-
anism for all conditions, and closely matched the extinction turning points. In addition, Figure 11 demonstrates the predictive ability of both the skeletal and reduced mechanisms in calculations of the laminar flame speeds, for pressures of 1, 20, and 40 atm, equivalence ratios ranging over 0.65–1.35, and an unburned gas temperature of 400K. Although some discrepancy is apparent near stoichiometric conditions for 1 atm, the maximum error is only 4.9\% for $\phi = 1.0$; at higher pressures, the calculations of the skeletal and reduced mechanisms are indistinguishable from those of the detailed mechanism.

Conclusions

Skeletal and reduced mechanisms for the LLNL gasoline surrogate were generated using a combined strategy of skeletal reduction via the DRGEPSA method followed by further unimportant reaction elimination, isomer lumping, and finally time-scale reduction based on the QSS assumption using CSP analysis. Starting with the original detailed mechanism with 1388 species and setting an error limit of 10\%, skeletal and reduced mechanisms were generated with 213 and 148 species, respectively, for a lean, low-temperature HCCI-like range of conditions, and 97 and 79 species, respectively, for a lean-to-rich, high-temperature SI/CI-like range of conditions. Validation of both reduced mechanisms showed good performance in predicting homogenous autoignition delay over the appropriate ranges of conditions. For the HCCI-like range of conditions, the associated skeletal and reduced mechanisms also performed well in more rigorous validation studies using temperature profiles in constant-volume autoignition simulations. Similarly, the SI/CI skeletal and reduced mechanisms closely matched the PSR temperature response curves and extinction turning points as well as the laminar flame speeds of the starting detailed mechanism. For both ranges of conditions, the final reduced mechanisms are compact enough to be used in multidimensional engine simulations while still capable of predicting relevant combustion properties nearly as well as the much larger detailed mechanism.

In addition to the skeletal and reduced mechanisms produced through the course of this study, improvements and observations were made regarding the reduction procedure itself. A new greedy sensitivity analysis algorithm for DRGEPSA was demonstrated, and shown to be capable of eliminating a larger number of species for the same error limit as the previous algorithm. Furthermore, we found that this algorithm, combined with the addition of PSR data to the reduction process and a high value for the sensitivity analysis cutoff threshold, produced a notably smaller skeletal mechanism that also performed well in autoignition, PSR, and laminar flame speed calculations. Additional investigation is warranted for the development of an automated, robust selection approach for the optimal CSP cutoff threshold; the ad hoc, manual selection method used previously may result in a poorly performing reduced mechanism under certain conditions.

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Supporting Information Available

The skeletal and reduced mechanisms for the gasoline surrogate generated for both HCCI and SI/CI engine conditions will be made available as supplementary material upon acceptance for publication. The new version of the MARS reduction package—including the greedy sensitivity analysis algorithm and the use of PSR simulations—is available upon request from the authors. This material is available free of charge via the Internet at [http://pubs.acs.org/](http://pubs.acs.org/).

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Table 1: Set of initial conditions used to generate skeletal mechanisms for the LLNL gasoline surrogate. Adopted from that used by Mehl et al.\textsuperscript{[7]}

| $\phi$ | $T$ (K) | $P$ (atm) |
|-------|---------|-----------|
| 1.0   | 800     | 10        |
| 1.0   | 750     | 60        |
| 0.6   | 1200    | 60        |
| 0.6   | 1100    | 10        |
| 0.6   | 1000    | 60        |
| 0.6   | 800     | 10        |
| 0.6   | 750     | 10        |
| 0.6   | 750     | 60        |
| 0.2   | 800     | 60        |
| 0.2   | 700     | 20        |
| 0.2   | 800     | 20        |

Table 2: Summary of results from mechanism reduction stages for HCCI-like target range of conditions. The reaction number discrepancy between the isomer lumping and CSP/QSS stage resulted from the need to convert reversible reactions into two irreversible reactions.

| Stage       | # Species | # Reactions | Max. error |
|-------------|-----------|-------------|------------|
| Detailed    | 1388      | 5933        |            |
| DRGEP       | 471       | 2434        | 3.8 %      |
| (Greedy) SA | 233       | 1061        | 8.9 %      |
| Reac. elim  | 233       | 910         | 8.3 %      |
| Isomer lump | 213       | 910         | 9.5 %      |
| CSP/QSS     | 148 (65 QSS) | 1809     | 9.3 %      |
Table 3: Lumped isomer groups selected for HCCI-like mechanism reduction. Refer to Mehl et al.\textsuperscript{6,7} for the species nomenclature.

| Group          | Isomers                                                                 |
|----------------|-------------------------------------------------------------------------|
| $C_7H_{14}OOH-O_2$ | $C_7H_{14}OOH1-3O_2$, $C_7H_{14}OOH2-4O_2$, $C_7H_{14}OOH3-5O_2$, $C_7H_{14}OOH4-2O_2$ |
| NC$7$KET       | NC$7$KET13, NC$7$KET24, NC$7$KET32, NC$7$KET35, NC$7$KET42             |
| $C_8H_{16}OOH$  | AC$8$H$_{16}$OOH-B, AC$8$H$_{16}$OOH-C, BC$8$H$_{16}$OOH-A, DC$8$H$_{16}$OOH-B |
| $C_8H_{16}OOH-O_2$ | AC$8$H$_{16}$OOH-BO$_2$, BC$8$H$_{16}$OOH-AO$_2$, DC$8$H$_{16}$OOH-BO$_2$ |
| IC$8$KET       | IC$8$KETAB, IC$8$KETBA, IC$8$KETBD, IC$8$KETDB                        |
| $C_7H_{15}O_2$  | $C_7H_{15}O_2$-1, $C_7H_{15}O_2$-2, $C_7H_{15}O_2$-3, $C_7H_{15}O_2$-4 |
| $C_8H_{17}O_2$  | AC$8$H$_{17}$O$_2$, BC$8$H$_{17}$O$_2$, DC$8$H$_{17}$O$_2$             |

Table 4: Comparison of various reduction parameters and results for SI/CI reduction, where “PSR” indicates the use of PSR data in the reduction. All skeletal reductions used a 10% error limit.

| SA Algorithm       | $\varepsilon^*$ | PSR | # Species |
|--------------------|------------------|-----|----------|
| Initially informed | 0.5              | yes | 330      |
| Greedy             | 0.5              | yes | 98       |
| Initially informed | 0.1              | no  | 249      |
| Greedy             | 0.1              | no  | 137      |
| Initially informed | 0.01             | no  | 315      |
| Greedy             | 0.01             | no  | 314      |

Table 5: Summary of results from mechanism reduction stages for SI/CI-engine target range of conditions. The reaction number discrepancy between the isomer lumping and CSP/QSS stage resulted from the need to convert reversible reactions into two irreversible reactions.

| Stage             | # Species | # Reactions | Max. error |
|-------------------|-----------|-------------|------------|
| Detailed          | 1388      | 5933        |            |
| DRGEP             | 415       | 2362        | 8.4%       |
| (Greedy) SA       | 98        | 802         | 9.1%       |
| Reac. elim        | 98        | 513         | 9.3%       |
| Isomer lump       | 97        | 512         | 9.5%       |
| CSP/QSS           | 79 (18 QSS)| 1018        | 11.5%      |
Figure 1: Autoignition validation of the DRGEPSA-produced skeletal mechanisms for the LLNL gasoline surrogate, corresponding to a 10% error limit, over a range of initial temperatures and pressures and at $\phi = 0.5$ in air. The skeletal mechanisms with 344 and 233 species were generated using the initially informed and greedy sensitivity analysis algorithms, respectively.

Figure 2: Number of QSS species as a function of CSP cutoff threshold $\epsilon_{\text{CSP}}$ for HCCI-like range of conditions.
Figure 3: Autoignition validation of the DRGEPISA-produced skeletal mechanisms generated using a 10% error limit for the LLNL gasoline surrogate in air at high temperatures relevant to SI/CI conditions, over a range of initial temperatures and pressures and at $\phi = 1.0$. The skeletal mechanisms with 330 and 98 species were generated using the initially informed and greedy sensitivity analysis algorithms, respectively.

Figure 4: Number of QSS species as a function of CSP cutoff threshold $\varepsilon_{CSP}$ for the SI/CI-like range of conditions.
Figure 5: Autoignition validation of the skeletal (213 species) and reduced (148 species) mechanisms for the LLNL gasoline surrogate targeted at HCCI-like conditions. Ignition delays were calculated over a range of initial temperatures, pressures, and equivalence ratios.
Figure 6: Comparison of temperature profiles for various initial temperatures at 10 atm and $\phi = 0.6$ calculated by the detailed mechanism and skeletal (213 species) and reduced (148 species) mechanisms targeted at HCCI-like conditions.

Figure 7: Comparison of temperature profiles for various initial temperatures at 40 atm and $\phi = 1.0$ calculated by the detailed mechanism and skeletal (213 species) and reduced (148 species) mechanisms targeted at HCCI-like conditions.
Figure 8: Comparison of temperature profiles for various initial temperatures at 60 atm and $\phi = 0.2$ calculated by the detailed mechanism and skeletal (213 species) and reduced (148 species) mechanisms targeted at HCCI-like conditions.
Figure 9: Autoignition validation of the skeletal (97 species) and reduced (79 species) mechanisms for the LLNL gasoline surrogate targeted at SI/CI-engine conditions. Ignition delay times were calculated over 1000–1600 K; 1, 20, and 40 atm; and equivalence ratios of 0.5–1.5 in air.
Figure 10: Comparison of PSR temperature response curves for the detailed, skeletal (97 species), and reduced (79 species) gasoline surrogate mechanisms generated using SI/CI conditions for pressures of 1, 20, and 40 atm; equivalence ratios of 0.5–1.5; and an inlet temperature of 300 K.
Figure 11: Comparison of laminar flame speeds calculated by the detailed, skeletal (97 species), and reduced (79 species) gasoline surrogate mechanisms generated using SI/CI conditions for a range of equivalence ratios at 1, 20, and 40 atm and an unburned gas temperature \( T_u = 400 \text{ K} \).