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# Skeletal mechanism generation for surrogate fuels using directed relation graph with error propagation and sensitivity analysis

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ABSTRACT

A novel implementation for the skeletal reduction of large detailed reaction mechanisms using the directed relation graph with error propagation and sensitivity analysis (DRGEPSA) is developed and presented with examples for three hydrocarbon components, *n*-heptane, *iso*-octane, and *n*-decane, relevant to surrogate fuel development. DRGEPSA integrates two previously developed methods, directed relation graph-aided sensitivity analysis (DRGASA) and directed relation graph with error propagation (DRGEP), by first applying DRGEP to efficiently remove many unimportant species prior to sensitivity analysis to further remove unimportant species, producing an optimally small skeletal mechanism for a given error limit. It is illustrated that the combination of the DRGEP and DRGASA methods allows the DRGEPSA approach to overcome the weaknesses of each, specifically that DRGEP cannot identify all unimportant species and that DRGASA shields unimportant species from removal. Skeletal mechanisms for *n*-heptane and *iso*-octane generated using the DRGEP, DRGASA, and DRGEPSA methods are presented and compared to illustrate the improvement of DRGEPSA. From a detailed reaction mechanism for *n*-alkanes covering *n*-octane to *n*-hexadecane with 2115 species and 8157 reactions, two skeletal mechanisms for *n*-decane generated using DRGEPSA, one covering a comprehensive range of temperature, pressure, and equivalence ratio conditions for autoignition and the other limited to high temperatures, are presented and validated. The comprehensive skeletal mechanism consists of 202 species and 846 reactions and the high-temperature skeletal mechanism consists of 51 species and 256 reactions. Both mechanisms are further demonstrated to well reproduce the results of the detailed mechanism in perfectly-stirred reactor and laminar flame simulations over a wide range of conditions. The comprehensive and high-temperature *n*-decane skeletal mechanisms are included as supplementary material with this article.


## 1. Introduction

Combustion of hydrocarbon fuels currently provides 85% of the energy produced in the United States [1,2]. Renewable sources of energy are being pursued to supplement and eventually replace combustion-based sources, but hydrocarbons will remain the major component for the next few decades. In the current era of increasing environmental awareness and rising fuel costs, there is considerable demand to improve efficiency and reduce emissions of the next generation combustion technology. Fuel-flexible designs that can use both conventional and alternative fuels are also desired.

Since computational modeling drives the design of engines and combustors for aerospace, transportation, and energy applications, accurate prediction of fuel combustion and pollutant emissions requires comprehensive detailed reaction mechanisms [3]. Liquid transportation fuels contain varying blends of many hydrocarbons. There has been a recent collaborative effort to develop surrogate models to emulate real fuels to accurately predict combustion properties. Such surrogate models typically contain mixtures of a small number of appropriate liquid hydrocarbons. However, detailed reaction mechanisms for surrogates of gasoline [4,5], diesel [6,5], and jet fuels [7–9] typically contain large numbers of species and reactions. For instance, a recently developed detailed mechanism for $C_8 - C_{16}$ *n*-alkane hydrocarbons contains 2115 species and 8157 reactions [10], while a mechanism for methyl-decanoate, a biodiesel surrogate, contains 2878 species and 8555 reactions [11]. Despite rapid advancements in computing power, it is generally formidable to integrate such detailed reaction mechanisms into large-scale computational simulations in terms of CPU time and memory requirements. Since the computational cost of chemistry scales by the third power of the number of species in the worst case when factorizing the Jacobian [12], such large sizes pose

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problems even in zero-dimensional modeling. In addition, the wide range of time scales (from nanosecond to second) and the nonlinear coupling between species and reactions induces stiffness when governing equations are solved [12]. Due to these computational demands, reduction of large mechanisms is necessary to facilitate practical simulations using realistic chemistry with modern computational tools.

Skeletal reduction is typically the first step of mechanism reduction, where species and reactions deemed negligible to important phenomena over the range of conditions of interest (e.g., pressure, temperature, and equivalence ratio) are removed from the detailed mechanism. Much effort has been dedicated to the development of effective skeletal reduction techniques, as reviewed by Griffiths [13], Tomlin et al. [14], and Okino and Mavrovouniotis [15]. Classical skeletal reduction methods include sensitivity analysis [16–18], principal component analysis [19], and detailed reduction [20]. Other important methods include lumping [21–23], genetic algorithms [24,25], optimization [26–28], and adaptive reduction approaches [29–33].

While mechanism reduction via time scale analysis is a separate approach outside the scope of this paper, such methods can be employed to perform skeletal reduction as well. Computational singular perturbation (CSP)-based methods [34–36] analyze the Jacobian matrix to decompose species relations into fast and slow components. Species are considered important if coupling is strong in either the fast or slow subspace. However, this approach can overestimate the importance of some species and produce skeletal mechanisms of larger size than other methods [37]. Another method similar to CSP is level of importance (LOI) analysis [38,29,39,40], which combines time scale analysis with sensitivity analysis to rank species importance. The most recent work [40] using LOI presented skeletal mechanisms for ethylene that are competitive with those generated using other methods [41], though the range of conditions considered in the LOI analysis was much narrower.

The chemistry-guided reduction (CGR) [42] approach was recently presented and applied to a detailed mechanism for *n*-heptane [43]. This method combines lumping and necessity analysis applied to a compact starting mechanism. The necessity of species is based on reaction-flow analysis toward and from important species. Though the resulting mechanism sizes are competitive with those from other methods (and the current work), CGR is not explicitly error-controlled and the emphasis on a small starting mechanism could be a possible limitation of the method.

Nagy and Turányi [44] developed the simulation error minimization connectivity method, based on the original connectivity method proposed by Turányi [18], which exhaustively analyzes sets of important species through Jacobian analysis and selects an optimal mechanism based on an error limit. The method was shown to provide minimal mechanism sizes for a given error but at a computational expense an order of magnitude above other methods [44]. This could limit the applicability of the approach to the particularly large mechanisms considered in the current work.

The directed relation graph (DRG) method, originally proposed by Lu and Law [41,45,37], recently received significant attention. This approach uses a directed graph to map the coupling of species and consequently find unimportant species for removal based on selected target species and an acceptable error threshold. It has been shown to be a particularly efficient and reliable method to reduce large reaction mechanisms [45]. Further development of the DRG method branched into two major directions: (1) DRG-aided sensitivity analysis (DRGASA) [46,47], from the original authors of the DRG method which performs sensitivity analysis on species not removed by DRG to further reduce the mechanism and (2) DRG with error propagation (DRGEP) [48], which considers the propagation of error due to species removal down graph pathways. Another method based on DRG, path flux analysis [49], was recently presented that uses both production and consumption fluxes to define the directed graph and identify important species. In the current work an approach that integrates the major aspects of DRGEP and DRGASA, DRG with error propagation and sensitivity analysis (DRGEPSA), is presented. It is illustrated that this combined approach overcomes the weaknesses of the two individual methods. The DRGEPSA method was initially presented by Raju et al. [50] and more recently by Niemeyer et al. [51,52]. We also note that a similar method combining DRGEP and DRGASA was also recently presented by Zsély et al. [53] for the ignition of natural gas mixtures, though not explored in detail as in the current work.

In the following, the methodology and implementation of DRGEPSA for the skeletal reduction of large detailed reaction mechanisms is first discussed in Section 2. In particular, neat components important to surrogates of gasoline, diesel, and jet fuels are considered. The weaknesses of DRGEP and DRGASA, and the subsequent improvement of DRGEPSA, are demonstrated with a skeletal reduction of the *n*-heptane detailed mechanism of Curran et al. [54,55] in Section 3.1. Additional comparisons are then made in Section 3.2 using a skeletal reduction of the *iso*-octane detailed mechanism of Curran et al. [55] A skeletal mechanism for *n*-decane from the detailed mechanism of Westbrook et al. [10] covering a wide range of conditions is presented in Section 3.3. In addition, a high-temperature skeletal mechanism is presented to illustrate the capability of the DRGEPSA method for reduction based on a specific range of conditions. Conclusions based on the various skeletal reductions as well as suggestions for future work are given in Section 4.

## 2. Methodology

The current reduction procedure begins with simulations of constant volume autoignition using the detailed reaction mechanism. The chemical kinetics data are sampled densely during the ignition evolution and used for the subsequent analysis while the ignition delay results are used to assess the overall performance of the resulting skeletal mechanism. The DRGEPSA formulation is integrated into the Mechanism Automatic Reduction Software (MARS) implementation [56], which provides a framework for combining multiple mechanism reduction methods into an automatic reduction scheme with minimal required user input.

The DRGEP method is first performed iteratively using the error in ignition delay prediction of the initial skeletal mechanism compared to the results using the detailed mechanism. The threshold used to identify and remove unimportant species is increased until the maximum error in ignition delay prediction for the given conditions reaches a user-specified limit. In this manner, the algorithm finds a minimally reduced skeletal mechanism with DRGEP. The remaining species are then divided into two groups: (1) "limbo" species for sensitivity analysis and (2) important species for automatic retention. Sensitivity analysis is performed on the limbo species to further identify unimportant species, which are then removed until the global ignition delay error reaches the user-specified limit. In all steps of the reduction process, reactions containing removed species are also eliminated from the mechanism. Specifics of each phase of the skeletal reduction and the DRGEPSA implementation are detailed as follows.

### 2.1. DRGEP phase

The first phase of DRGEPSA is based on the DRGEP of Pepiot-Desjardins and Pitsch [48], which in turn is an extension of the original DRG of Lu and Law [41,45,37]. The current DRGEP implementation includes an improved definition of the direct interaction