Development of a Reduced Four-Component (Toluene/n-Heptane/iso-Octane/Ethanol) Gasoline Surrogate Model

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Abstract

The prospect of blending gasoline fuel with ethanol is being investigated as a potential way to improve the knock resistance of the base gasoline. However, one of the drawbacks is a lack of proper understanding of the reason for the non-linear response of blending ethanol and gasoline. This non-linearity could be better understood by an improved knowledge of the interactions of these fuel components at a molecular level. This study proposed a highly reduced four-component (toluene/n-heptane/iso-octane/ethanol) gasoline surrogate model containing 59 species and 270 reactions. The model was reduced using the direct relation graph with expert knowledge (DRG-X) [1, 2] and isomer lumping method. The computational singular perturbation (CSP) analysis were performed to reduce the potential stiffness issues by accordingly adjusting the Arrhenius coefficients of the proper reactions. The model has been comprehensively validated against wide range of ignition delay times (IDT) and flame speed (FS) measurement data as well as compared against two representative literature models from Liu et al. [3] and Wang et al. [4]. Overall, good agreements were observed between model predictions and experimental data across the entire research octane number (RON), equivalence ratio, pressure and temperature range. In addition, the model has also been coupled with the computational fluid dynamic (CFD) models to simulate the experimental data of constant volume reacting spray of a low-octane gasoline (Haltermann straight-run naphtha), and in-cylinder pressures and temperatures of a high-octane gasoline (Haltermann Gasoline) combustion in a heavy duty compression ignition engine. The coupled model can qualitatively predict the experimentally obtained data with an improved performance for PRF, TPRF, and TPRF-ethanol surrogates.

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1. Introduction

Recent review papers by Kalghatgi et al. [5, 6] emphasized the essential role of the internal combustion engines (ICEs) in transportation sector in the foreseeable future. The use of gasoline fuels in spark ignition (SI) and compression ignition (CI) engines [7] can be improved by following a systematic fuel design approach linking combustion fundamentals with computational engineering and design. From a combustion perspective, one of the main challenges is to co-optimize engine and fuel to achieve both high efficiency and low emissions. Commercial fuels like gasoline, diesel, aviation kerosene etc. are complex mixtures of hundreds to thousands of hydrocarbons and oxygenated chemical species; therefore, simple and reliable surrogate mixtures are required to represent the corresponding commercial fuels for the further experimental or computational studies coupled with practical engines. The simplest and most widely used gasoline surrogates are Primary Reference Fuel (PRF) and Toluene Primary Reference Fuel (TPRF) surrogates, which are binary mixtures of iso-octane and n-heptane, and ternary mixtures of PRF plus toluene. Sarathy et al. [7] reviewed the gasoline surrogate formulation approaches and the experimental and chemical kinetic studies on the relevant surrogates. Among these approaches, Kalghatgi et al. [8, 9] developed a method to define the composition of a TPRF by matching both research octane number (RON) and motor octane number (MON) of a target gasoline. Ahmed et al. [10] presented a computational method for formulating multicomponent surrogates by matching the fuel properties such as hydrogen/carbon (H/C) ratio, density, distillation characteristics, carbon types, RON etc. Jameel et al. [11] demonstrated a novel approach for surrogate formulation by emulating the functional groups of target gasoline fuels, while minimizing the number of surrogate species.

Nowadays, the use of oxygenated gasolines, such as blending oxygenates, methyl tertiary-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), and ethanol added to regular gasoline, has grown significantly, as an attempt to improve the anti-knock quality [12] and to reduce the lifecycle (well-to-wheel) CO₂ emission [13]. Lee et al. [14] performed the experimental and kinetic modelling studies of the auto-ignition behavior of two oxygenated certification gasolines: Haltermann (RON = 91) and Coryton (RON = 97.5). In this study, a quaternary surrogate (iso-octane, n-heptane, toluene and

ethanol) was formulated to simulate the experimental results using detailed chemical kinetic model, and it was proved to be a promising surrogate which can reproduce the IDT of both fuels, especially for Coryton gasoline which has a high octane sensitivity ($S = \text{RON} - \text{MON}$).

A comprehensive literature review has been done regarding the reduced gasoline surrogate models published since 2000, they have been summarized in Table S1 in the Supplementary Material. The type of surrogates varies from the simplest two-component (iso-octane/n-heptane) PRF, three-component (toluene/iso-octane/n-heptane) TPRF, and additional multi-component surrogates. The size of model varies from dozens of species and hundreds to thousands of reactions. These models were validated against different targets including ignition delay times (IDT), flame speeds (FS), speciation profiles measured from flow reactors and premixed flames under different conditions.

Most recently, Sarathy et al. [15] presented a skeletal TPRF model with 76 species and 401 reactions, which was developed using the direct relation graph with expert knowledge (DRG-X) [1, 2] and isomer lumping method. Building on this model, the present study aims to develop a four-component (toluene/n-heptane/iso-octane/ethanol) – TPRF-Ethanol gasoline surrogate model with even fewer number of species and reactions for use in more computationally demanding multi-dimensional CFD model. This model has been systematically validated against a wide range of IDT and FS measurement data available in literature. In addition, the developed kinetic model was then implemented in CFD simulations of a low-octane gasoline combustion in both constant volume reactor and heavy duty compression ignition engine. All the simulation results were compared against the results by Liu et al. [3] and Wang et al. [4].

2. Computational Methods

Model reduction approach

In our previous study [15], a three component TPRF kinetic model with 80 species and 414 reactions (including NO_x) is developed and fully validated. Here, the goal is to develop a four-component TPRF-E model with a smaller number of species and reactions for multi-dimensional CFD

applications. Targeted conditions include low, intermediate and high-temperature chemistry regimes that are encountered in engine combustion.

First, a skeletal ethanol sub-mechanism was added to the recently developed TPRF model in [15], which was generated manually, which includes three more species: $\text{C}_2\text{H}_5\text{OH}$, $\text{SC}_2\text{H}_4\text{OH}$ and CH_3CHO , and the relevant high temperature reaction classes (H-atom abstraction and radical beta-scission). Combined, the detailed TPRF + ethanol mechanism consists of 83 species, which was further reduced to 59 species using a second round of DRG-X reduction [2].

As reported in [15], decoupling approach is based on the assumption that heat release, flame speeds, extinction and emissions of unburnt HC, CO & NO_x strongly depend on the chemistry of $\text{H}_2/\text{CO}/\text{C}_1$ and that of small radicals. These properties could be predicted by inclusion of detailed $\text{H}_2/\text{CO}/\text{C}_1$ mechanism and reduced $\text{C}_2\text{--C}_3$ mechanism. In DRG-X, it is assumed that some species are weakly coupled to others, so they have little contributions to the reaction pathways and thus can be eliminated [2, 16-18]. A list of starting species is first developed, and then all species that are irrelevant to the species are removed based on a user-specified error threshold. Additional conditions of interest, such as the equivalence ratios, temperature and pressure are specified. In this study, targeted conditions for reduction include: high/low temperature (600 – 1300K), high pressure (5-50atm); lean to rich equivalence ratio and the error for heat release is specified as 0.5.

Stiffness analysis with computational singular perturbation

The development procedure of the introduced reduced model included a stiffness analysis. The main goal of this step was to reduce as much as possible the model's stiffness by accordingly adjusting the Arrhenius coefficients of the proper reactions, i.e., the reactions contributing to the generation of the fastest chemical timescales. This tuning procedure is of paramount importance, since the fastest chemical timescales are those that control the necessary time step in explicit solvers of computational fluid dynamics (CFD) codes. As a result, the faster the chemical timescales, the more expensive the simulation's computational cost. Despite its high significance, this procedure is not commonly

practiced in the community as of today. To our knowledge, this is the first study to formally follow the procedure during the development of a reduced chemical kinetics model.

The analysis was performed in the general framework of the computational singular perturbation (CSP) approach [1, 19], an algorithmic method of asymptotic analysis which has been successfully employed in the context of reacting flows for model reduction [20-23], for the identification of the key processes and species in auto-igniting systems [24-33] and flames [34-36] and for the characterization of the flame topology in the context of DNS [37, 38].

According to the CSP theory, the system of the species N and energy governing equations is transformed into a new form by means of the CSP basis vectors, which in the current study are approximated by the right eigenvectors of the Jacobian J of the chemical source term [1, 19]. In the CSP form, the system is decomposed into $N+1$ CSP modes. Each of the CSP modes is described by two quantities: (i) a timescale, which sets the timeframe of the action of that mode and (ii) an amplitude, which signifies the impact of that mode to the system's slow evolution. The timescale of the i -th mode can be approximated by the inverse norm of the related i -th eigenvalue, i.e., $\tau_i = \frac{1}{|\lambda_i|}$ [1, 19]. The positive and negative real parts of the eigenvalues represents explosive and dissipative nature of the process, respectively. By definition, fast timescales relate to eigenvalues with large norms. The timescale participation index (TPI) is an algorithmic tool which identifies the chemical reactions that contribute to the generation of each timescale/eigenvalue [24-33]. In the current study, the TPI tool has been used in order to identify the reactions that contribute to the generation of the system's fastest chemical timescales. Considering the large dynamic range of the system's eigenvalues, their logarithmic scale is employed as follows:

$$\Lambda_i = \text{sign}(\lambda_i) \cdot \log_{10}|\lambda_i|$$

The stiffness analysis was performed after the completion of the reduction process using DRG and the isomer lumping methods. The produced reduced model was employed in zero-dimensional (0D) autoignition simulations in a wide range of initial conditions. In particular, the following conditions

were tested for various fuel blends of toluene/iso-octane/n-heptane/ethanol: $700K < T(0) < 1,500K$, $10 \text{ atm} < p(0) < 50 \text{ atm}$, $0.6 < \phi < 1.5$. Each one of the 0D simulations was analyzed through the CSP approach, in that, all system's eigenvalues were generated and the TPI tool was used in order to identify the reactions generating the eigenvalues with the largest norms. The analysis revealed that the set of the reactions generating the fastest timescales remained the same, regardless the different initial conditions.

Spray combustion simulations

The spray experiments were conducted in an optically accessible constant volume chamber at Michigan Technological University (MTU) [39, 40]. The chamber is a pre-burn type which uses a mixture of acetylene and hydrogen in an appropriate composition with oxygen and nitrogen for pre-burn. The fuel injection is timed during the cool-down phase of the pre-burn when an exact ambient condition was reached. Further details of the experimental facilities can be found in Zhang et al. [39] and Meng et al. [40]. The injector nozzle used was a single hole of outlet diameter $176 \mu\text{m}$ with k-factor of 1.8 and discharge coefficient of 0.94 at $\text{Re} = 12000$.

The spray combustion simulations were performed using commercial finite volume based CFD code CONVERGETM. The spray break-up was modeled using the modified Kelvin-Helmholtz and Rayleigh-Taylor (KH-RT) model without an ad-hoc break-up length. In addition, blob injection atomization model, NTC droplet collision model, Post collision outcome model, and Frossling evaporation models were used. For turbulence modeling, Renormalization group (RNG) k- ϵ model was used. Further details of the models used can be found in Mohan et al. [41] and Pei et al [42]. The fuel liquid properties used in the simulations were generated using Aspen HYSYS. These properties have been extensively validated in the previous studies.

The computational domain is a cube of side 100 mm. The mesh was generated during runtime by the CFD code. The base grid size of 2 mm is used along with a level 4 fixed embedding of injector type and adaptive mesh refinement (AMR) of level 4 was employed for velocity, temperature, and fuel

species fields. Figure 1 shows the base mesh, fixed embedding, and AMR generated by the CFD code at 0.5 ms After the Start Of Injection (ASOI).

Figure 1. Grid generated by CONVERGE™ at 0.5 ms ASOI

Engine combustion simulations

A single cylinder 4 valve engine with a 16:1 volumetric compression ratio (CR) is used in this investigation. Table 1 shows the details of the engine specifications and more details about the engine can be found in [43, 44]. A new set of CR 16 piston was designed and used here to accommodate the PPC combustion strategy using a commercial gasoline with research octane number (RON) of 91. The fuel used in this study is the CARB LEV III E10 certification gasoline and some of its properties are listed in Table 2. A low-load operating point is used here for model validation. The low-load point details are listed in Table 3. This point was chosen because the combustion mode at these operating

conditions is governed by sequential autoignitions of the partially premixed fuel/air in-cylinder mixtures and this poses a challenge of the robustness of chemical kinetic models.

Table 1 Single cylinder engine specifications.

Cylinders	1
Number of Valves	4
Displacement (L)	0.55
Bore (mm)	86
Stroke (mm)	94.6
Connecting Rod (mm)	148
CR	14.5:1
Fuel Injector	Centrally mounted, multi-hole GDI
Spray angle (°)	130
Number of nozzles	10
Nozzle diameter (mm)	0.165

Table 2 Properties of the RON91 gasoline.

RON	91
MON	83.4
S	7.6
H/C	1.97
Lower heating value (MJ/kg)	41.9
Oxygenates (vol.%)	8.2
Paraffins (vol.%)	13.4
Iso-paraffins (vol.%)	33.7
Olefins (vol.%)	6.8
Naphthenes (vol.%)	15.2
Aromatics (vol.%)	22.7

IBP (°C)	41.1
T10 (°C)	58.9
T50 (°C)	101.6
T90 (°C)	158.3
FBP (°C)	176.1

Table 3 Engine operating and boundary conditions.

IMEP (bar)	6
RMP	1500
Intake pressure (bar)	1.5
Intake Temperature (K)	331
SOI (CAD aTDC)	-40
Injection pressure (bar)	51
Fuel temperature (K)	363
Exhaust gas recirculation (EGR) (%)	0
Fuel mass (mg/cycle)	16.49
Spray angle (°)	130
Plume angle (°)	15
Number of nozzles	10
Nozzle diameter (mm)	0.142

CONVERGE v2.4 [45] was used to perform the CFD simulations in this work. CONVERGE is a general purpose CFD code to solve multi-dimensional reacting flows with stationary and moving boundaries. More detailed descriptions of the models can be found in [45]. The RANS-based turbulent renormalization group (RNG) k- ϵ model was utilized throughout the simulations. A Lagrangian spray model based on the blob injection model of Reitz and Diwakar [46] was used, wherein computational parcels of liquid with a characteristic size equal to the effective nozzle diameter were introduced into the computational domain. The spray breakup models were implemented based on the recommendations from the constant volume chamber simulations [43, 44]. More details about the

spray models and the validations against engine combustion network (ECN4) spray G [47] can be found in [43, 44].

3. Results and discussions

3.1. Stiffness analysis

Figure 2 displays a typical example of the system's temporal evolution of the fastest timescales (grey circles) along with temperature (red-dashed line) against time scaled with the ignition delay time, for 30%iso-octane/30%n-heptane/20%toluene/20%ethanol/air, $T(0) = 800\text{K}$, $p(0) = 20\text{atm}$, $\varphi = 0.6$. It is shown that after ignition $\Lambda_1 < -15$, corresponding to a timescale faster than 1 femtosecond (fs), which can be considered a non-physical value. In addition, there is a large gap between Λ_2 and Λ_3 for the most part of the process, suggesting that a potential decrease of that gap would decrease significantly the computational cost in integration solvers of explicit type. Thus, the first two fastest timescales (Λ_1 and Λ_2) were investigated further and the reactions shown in Table 4 were identified by the TPI tool to contribute the most to the large norms of Λ_1 and Λ_2 . As a result, the Arrhenius coefficients of those reactions were gradually revised (decreased) in an iterative fashion so that the gap between Λ_2 and Λ_3 was minimized and the large norm of Λ_1 after ignition was significantly decreased as shown by the green signs in Figure 2, with a sufficiently small impact to the model's accuracy at all operating conditions. It is noted that in the original version of the mechanism, no Arrhenius coefficients were provided for 38b and its rate constant was calculated based on the respective forward and equilibrium constants while after the revision, Arrhenius coefficients were explicitly provided. Figure 2 shows that as a result of this refining procedure, the norm of fastest eigenvalue (i.e, Λ_1) was decreased by approximately two orders of magnitude in the cold region and roughly three orders of magnitude in the hot region, after ignition.

Figure 2. The smallest eigenvalues (largest norms) and temperature profiles using the original (grey and red colors) and the revised (green and blue colors) Arrhenius coefficients for the reactions in Table 4, during the autoignition of 30%iso-octane/30%n-heptane/20%toluene/20%ethanol/air, $T(0) = 800$ K, $p(0) = 20$ atm, $\phi = 0.6$. In both cases, time has been scaled against the ignition delay time.

Table 4: The reactions identified by the TPI tool to generate the first two fastest timescales, along with their original and revised Arrhenius coefficients.

#Rxn	Description	Original values			Revised values		
		A	b	Ea	A	b	Ea
3f	$C_6H_5CH_2 + OH \rightarrow C_6H_5CHO + H_2$	$2.11E + 19$	1.0	0.0	$3.0E + 14$	0.0	0.0
4f	$C_6H_5CH_2 + HO_2 \rightarrow C_6H_5CHO + H_2O$	$2.11E + 19$	0.0	0.0	$3.0E + 14$	0.0	0.0
40f	$C_8H_{16}OOH + O_2 \rightarrow C_8H_{16}OOH - O_2$	$8.00E + 14$	0.0	0.0	$3.0E + 14$	0.0	0.0
38f	$C_8H_{17}O_2 \rightarrow C_8H_{16}OOH$	$2.86E + 11$	1.23	22,000	$2.86E + 11$	1.23	22,000
38b	$C_8H_{17}O_2 \leftarrow C_8H_{16}OOH$	-	-	-	$1.37E + 08$	1.28	6,835

In order to demonstrate further the success of this refining process, the produced model was compared to other models available in the literature. While a fair comparison would require all mechanisms to have the same number of species, by comparing the current model with larger and smaller in size models we aim to demonstrate the success of the approach followed. Figure 3 shows the stiffness performance of the current model after its revision against three TPRF models of

increasing number of complexity in terms of the included species and reactions: Liu's model [3], Sarathy's model [15] and Wang's model [4]. It is seen that the fastest of the chemical timescale (i.e., Λ_1) of the current model is considerably slower compared to Sarathy's and Wang's models (the larger ones) and slightly faster compared to Liu's model (the smaller one). Therefore, the present approach was able to reduce significantly the potential computational cost of the reaction source calculations using explicit solvers, making the introduced model ideal for usage in direct numerical simulations (DNS). This suggests that the computational cost of the current mechanism would be lower compared to Sarathy's and Wang's models, with the usage of an explicit solver.

Figure 3. The smallest eigenvalues (largest norms) and temperature profiles using the produced revised (green and blue colors) model and three other models (grey and red color) available in the literature; Liu's model [3] on the left, Sarathy's model [15] in the middle and Wang's model [4] on the right. In all cases, a homogeneous batch reactor was used with 40%iso-octane/40%n-heptane/20%toluene/air, $T(0) = 800$ K, $p(0) = 20$ atm, $\phi = 0.6$. Time has been scaled against the respective ignition delay times.

3.2. Ignition delay times (IDTs) validations

It is evident that the feasibility of a highly reduced kinetic model largely relies on the validations against the experimental data. To this end, comprehensive literature reviews have been done for the IDT measurements of relevant fuels, for pure component (iso-octane, n-heptane and toluene), ethanol

related mixture, gasoline surrogates and real gasolines oxidation, as shown in Table S2-S4 in the Supplementary Material. Among these, a comprehensive data matrix was selected for validations:

- Pure component (iso-octane, n-heptane, toluene and ethanol) [17, 48-51]
- PRF surrogate mixtures (PRF60, 70, 80, 84, 91 and 95) [52, 53]
- TPRFs surrogate mixtures (TPRF70, 80, 91 and 97.5) [54]
- PRF- and TPRF-ethanol surrogate mixtures [55, 56]
- Haltermann straight-run naphtha (HSRN) [57]
- A blend of low- and high-octane for gasoline compression ignition (GCI) engines (GCI Blend) [58]
- Haltermann gasoline [14]
- Coryton gasoline [14]

The selected data matrix covers a wide range of engine operating conditions:

- Research octane number (RON) from low to high (0 – 118)
- Fuel concentration or equivalence ratio from lean to rich (0.5 – 2.0)
- Pressures from low to high (10 – 60 atm)
- Temperatures from low to high (700 – 1300 K)

Correspondingly, the representative validation results were presented as following:

- Figure 4 Figure 9 show the validation results for the IDTs of PRF70, 91 and 95 surrogate mixtures oxidation [52, 53].
- Figure 10 Figure 15 show the validation results for the IDTs of TPRF70, 91 and 97.5 surrogate mixtures oxidation [54].
- Figure 16 Figure 17 show the validation results for the IDTs of PRF- and TPRF-Ethanol surrogate mixtures oxidation respectively [55, 56].
- Figure 18 Figure 21 show the show the validation results for the IDTs of HSRN oxidation using both PRF60 and TPRF60 surrogates [57].

- Figure 22Figure 23 show the show the validation results for the IDTs of GCI Blend oxidation using PRF77 surrogate [58].
- Figure 24Figure 25 show the show the validation results for the IDTs of Haltermann Gasoline oxidation using TPRF-Ethanol surrogate [14].
- Figure 26Figure 27 show the show the validation results for the IDTs of Coryton Gasoline oxidation using TPRF-Ethanol surrogate [14].

Because of the length limitation of the paper, the rest of validation results were presented in Figure S1-S12 in the Supplementary Material.

In these figures, the reactants' compositions were presented in the caption of each figure, and the results generated from current model were compared with the ones predicted by Liu et al. [3] and Wang et al. [4]. Symbols are experimental data. Note that this study focuses on the validations of IDT measured from shock tubes, which are all solid symbols. Different line shapes correspond to different models' predictions, and different colors correspond to different pressures or equivalence ratios.

Overall, good agreements were observed for the entire validation matrix, the proposed model can accurately reproduce the IDT data both at high temperature regime and negative temperature coefficient (NTC) regime. However, Wang's model predicts too fast IDT (greater than a factor of two) when simulating the TPRF mixtures, and both Liu and Wang's models are absent in ethanol sub-mechanism for the validations of PRF-ethanol and TPRF-ethanol surrogates.

Figure 4. IDTs validation of PRF70 oxidation at $\phi = 0.5$. Reactants' composition: 0.59% IC_8H_{18} , 0.28% NC_7H_{16} , 20.82% O_2 and 78.32% N_2

Figure 5. IDTs validation of PRF70 oxidation at $\phi = 1.0$. Reactants' composition: 1.16% IC_8H_{18} , 0.56% NC_7H_{16} , 20.64% O_2 and 77.64% N_2

Figure 6. IDTs validation of PRF91 oxidation at $\phi = 0.5$. Reactants' composition: 0.76% IC_8H_{18} , 0.08% NC_7H_{16} , 20.82% O_2 and 78.33% N_2

Figure 7. IDTs validation of PRF91 oxidation at $\phi = 1.0$. Reactants' composition: 1.51% IC_8H_{18} , 0.17% NC_7H_{16} , 20.65% O_2 and 77.68% N_2

Figure 8. IDTs validation of PRF95 oxidation at $\phi = 0.5$. Reactants' composition: 0.79% IC_8H_{18} , 0.05% NC_7H_{16} , 20.82% O_2 and 78.34% N_2

Figure 9. IDTs validation of PRF95 oxidation at $\phi = 1.0$. Reactants' composition: 1.57% IC_8H_{18} , 0.09% NC_7H_{16} , 20.65% O_2 and 77.69% N_2

Figure 10. IDTs validation of TPRF70 oxidation at $\phi = 0.5$. Reactants' composition: 0.35% IC_8H_{18} , 0.33% NC_7H_{16} , 0.27% $\text{C}_6\text{H}_5\text{CH}_3$, 20.80% O_2 and 78.25% N_2

Figure 11. IDTs validation of TPRF70 oxidation at $\phi = 1.0$. Reactants' composition: 0.69% IC_8H_{18} , 0.66% NC_7H_{16} , 0.54% $\text{C}_6\text{H}_5\text{CH}_3$, 20.61% O_2 and 77.52% N_2

Figure 12. IDTs validation of TPRF91 oxidation at $\phi = 0.5$. Reactants' composition: 0.29% IC_8H_{18} , 0.17% NC_7H_{16} , 0.54% $C_6H_5CH_3$, 20.79% O_2 and 78.21% N_2

Figure 13. IDTs validation of TPRF91 oxidation at $\phi = 1.0$. Reactants' composition: 0.57% IC_8H_{18} , 0.34% NC_7H_{16} , 1.08% $C_6H_5CH_3$, 20.58% O_2 and 77.43% N_2

Figure 14. IDTs validation of TPRF97.5 oxidation at $\phi = 0.5$. Reactants' composition: 0.09% IC_8H_{18} , 0.15% NC_7H_{16} , 0.84% $C_6H_5CH_3$, 20.77% O_2 and 78.14% N_2

Figure 15. IDTs validation of TPRF97.5 oxidation at $\phi = 1.0$. Reactants' composition: 0.17% IC_8H_{18} , 0.31% NC_7H_{16} , 1.67% $C_6H_5CH_3$, 20.55% O_2 and 77.30% N_2

Figure 16. IDTs validation of PRF-Ethanol oxidation at $\phi = 1.0$. Reactants' composition: 1.09% IC_8H_{18} , 0.35% NC_7H_{16} , 0.99% C_2H_5OH , 20.49% O_2 and 77.08% N_2

Figure 17. IDTs validation of TPRF-Ethanol oxidation at $\phi = 1.0$. Reactants' composition: 0.69% IC_8H_{18} , 0.21% NC_7H_{16} , 0.34% $C_6H_5CH_3$, 2.08% C_2H_5OH , 20.30% O_2 and 76.37% N_2

Figure 18. IDTs validation of HSRN oxidation at $p = 20$ atm using PRF60 surrogate.

Figure 19. IDTs validation of HSRN oxidation at $p = 60$ atm using PRF60 surrogate.

Figure 20. IDTs validation of HSRN oxidation at $p = 20$ atm using TPRF60 surrogate.

Figure 21. IDTs validation of HSRN oxidation at $p = 60$ atm using TPRF60 surrogate.

Figure 22. IDTs validation of GCI blend oxidation at $p = 20$ atm using PRF77 surrogate.

Figure 23. IDTs validation of GCI blend oxidation at $p = 40$ atm using PRF77 surrogate.

Figure 24. IDTs validation of Haltermann gasoline oxidation at $p = 20 \text{ atm}$ using TPRF-E surrogate.

Figure 25. IDTs validation of Haltermann gasoline oxidation at $\phi = 0.9$ using TPRF-E surrogate.

Figure 26. IDTs validation of Coryton gasoline oxidation at $p = 20$ atm using TPRF-E surrogate.

Figure 27. IDTs validation of Coryton gasoline oxidation at $\phi = 0.9$ using TPRF-E surrogate.

3.3. Flame speeds (FSs) validations

Similar to the IDTs validations, comprehensive literature reviews were also carried out for the FSs measurements of relevant fuels. A comprehensive literature review has been done for pure component (iso-octane, n-heptane, toluene and ethanol), gasoline surrogates and real gasolines oxidation, shown in Table S5-S6 in the Supplementary Material. Among these, a comprehensive data matrix was selected for validations:

- iso-Octane [59-66]
- n-Heptane [59-65, 67, 68]
- Toluene [59, 60, 69]
- Ethanol [63, 70, 71]
- iso-Octane and ethanol mixture [63]
- n-Heptane and ethanol mixture [63]
- PRFs (PRF50, 80, 87, 90 and 95) [61, 63, 65]
- PRF and ethanol mixture [63]

The selected data matrix covers wide range of conditions:

- Research octane number (RON) from low to high (0 – 118)
- Fuel concentration or equivalence ratio from lean to rich (0.6 – 1.7)
- Initial pressures from low to high (0.5 – 25 atm)
- Unburn gas temperatures from low to high (298 – 470 K)

Correspondingly, the validation results for the iso-octane/n-heptane/toluene/ethanol mixtures were presented as following:

- Figure 28 shows the validation results for the FSs of iso-octane and ethanol mixture [63].
- Figure 29 shows the validation results for the FSs of n-heptane and ethanol mixture [63].
- Figure 30Figure 32 show the validation results for the FSs of PRFs (PRF50, 80, 87, 90 and 95) [61, 63, 65]

- Figure 33 shows the validation results for the FSs of PRF and ethanol mixture [63].

Because of the length limitation of the paper, the validation results for the pure iso-octane, n-heptane, toluene and ethanol component were presented in Figure S13-S24 in the Supplementary Material.

In these figures, the results generated from current model were again compared with the ones predicted by two literature models from Liu et al. [3] and Wang et al. [4]. Symbols are experimental data, different line shapes correspond to different models' predictions, and different colors correspond to different experimental conditions: either different initial pressures or different unburn gas temperatures. Overall, good agreements were observed for the entire validation matrix, the proposed model was able to predict the FSs data across a range of equivalence ratios for different reactant mixtures. However, Liu's model performs too slow at fuel lean side and too fast at fuel rich side for almost all mixtures.

Figure 28. FSs validation of iso-octane and ethanol mixture oxidation at $p = 1$ atm.

Figure 29. FSs validation of n-heptane and ethanol mixture oxidation at $p = 1$ atm.

Figure 30. FSs validation of PRF50 oxidation at $p = 1$ atm.

Figure 31. FSs validation of PRF87 oxidation at $T_u = 373$ K.

Figure 32. FSs validation of PRF80, 90 and 95 oxidation at $T_u = 298$ K and $p = 1$ atm.

Figure 33. FSs validation of PRF and ethanol mixture oxidation at $p = 1$ atm.

3.4. Sensitivity, rate of production (ROP) and flux analyses

Sensitivity, rate of production (ROP) and flux analyses were carried out in order to show the reasonably detailed chemistry in this highly reduced model. Key reactions responsible for IDT targets and fuel consumption pathways were identified. Analyses in this section and the IDT and FS validations in next two sections were performed using ANSYS Chemkin 19.1 software package [72]. A TPRF-ethanol mixture (0.78% IC_8H_{18} , 0.28% NC_7H_{16} , 0.53% $\text{C}_6\text{H}_5\text{CH}_3$, 0.35% $\text{C}_2\text{H}_5\text{OH}$, 20.60% O_2 and 77.48% N_2) used as a Haltermann gasoline surrogate [14] was selected as a representative reactant for the sensitivity, ROP and flux analyses in this section, and simulations were performed in a constant-volume batch reactor.

The sensitivity coefficient of the basic sensitivity analyses for IDT targets were defined as:

$$S = \frac{\ln(\tau_+/\tau_-)}{\ln(k_+/k_-)} = \frac{\ln(\tau_+/\tau_-)}{\ln(2.0/0.5)}$$

where τ_+ and τ_- correspond to the IDTs calculated by increasing and decreasing the A-factor of every reaction rate by a factor of two respectively. A positive value of S indicates an inhibiting reaction and vice versa.

Figure 34 shows the sensitivity analysis results at $\phi = 0.9$ in air and $p = 40$ atm. The top-ten most relevant reactions that are sensitive to fuel and fuel radicals were highlighted at (a) $T = 1200$ and (b) $T = 800$ K, respectively. The typical reaction classes, such as alkyl radicals ($\dot{\text{C}}_8\text{H}_{17}$ and NC_7H_{15}) unimolecular decomposition, H-atom abstraction from weakly-bonded allylic- and α -sites ($\text{C}_6\text{H}_5\text{CH}_3 + \text{O}_2$ and $\text{C}_2\text{H}_5\text{OH} + \text{HO}_2$), alkylperoxy radicals ($\text{C}_8\text{H}_{17}\dot{\text{O}}_2$ and $\text{NC}_7\text{H}_{15}\text{OO}\dot{\text{O}}$) isomerization and concerted elimination, were identified as either promoting or inhibiting the reactivity.

Figure 35 shows the ROP analysis results at $\phi = 0.9$ in air and $p = 40$ atm. The concentration profiles of four reactants (IC_8H_{18} , NC_7H_{16} , $\text{C}_6\text{H}_5\text{CH}_3$ and $\text{C}_2\text{H}_5\text{OH}$) and pressure profiles were plotted in different colors at (a) $T = 1200$ and (b) $T = 800$ K, respectively. Flux analysis was performed at the time point of 0.035 and 0.7 ms respectively, where the four reactants were under rapid consumption process. The qualitative flux analysis results shown in Figure 36 demonstrates the reasonably detailed chemistry that has been included in this highly reduced model. Note that, the results have combined the reaction pathways at high-temperature ($T = 1200$ K) and low-temperature ($T = 800$ K) together, and for iso-octane and n-heptane oxidation, typical structures were presented for the lumped fuel radical ($\dot{\text{C}}_8\text{H}_{17}$ and NC_7H_{15}) and the subsequent radical pools.

(a) $T = 1200$ K

(b) $T = 800$ K

Figure 34. Sensitivity analysis for a TPRF-Ethanol mixture used as a Haltermann Gasoline surrogate (0.78% IC_8H_{18} , 0.28% NC_7H_{16} , 0.53% $C_6H_5CH_3$, 0.35% C_2H_5OH , 20.60% O_2 and 77.48% N_2), $\phi = 0.9$ in 'air' and $p = 40$ atm.

(a) $T = 1200$ K

(b) $T = 800$ K

Figure 35. ROP analysis for a TPRF-Ethanol mixture used as a Haltermann Gasoline surrogate (0.78% IC₈H₁₈, 0.28% NC₇H₁₆, 0.53% C₆H₅CH₃, 0.35% C₂H₅OH, 20.60% O₂ and 77.48% N₂), $\phi = 0.9$ in 'air' and $p = 40$ atm.

IC₈H₁₈: 0.78%

NC₇H₁₆: 0.28%

C₆H₅CH₃: 0.53%

C₂H₅OH: 0.35%

Figure 36. Flux analysis for a TPRF-Ethanol mixture used as a Haltermann Gasoline surrogate (0.78% IC₈H₁₈, 0.28% NC₇H₁₆, 0.53% C₆H₅CH₃, 0.35% C₂H₅OH, 20.60% O₂ and 77.48% N₂), $\phi = 0.9$ in 'air' and $p = 40$ atm.

3.5. Constant volume reacting spray related CFD simulations

Before we illustrate the CFD simulation results of HSRN ignition in the setup described above, the IDT validation of this practical fuel and PRF60 mixture using both PRF and TPRF surrogates in a homogenous reactor (shock tube) has been carried out under the condition of $\phi = 1.0$ and $p = 60$ atm, as shown in Figure 37. Figure 38 shows the CFD simulation results for the IDTs of HSRN fuel. The experimental conditions used for validation are the ambient pressure of 6 MPa, ambient temperature of 800, 900 and 1100 K, injection pressure of 150 MPa and 15% ambient oxygen. The ignition delay time is defined as the time until 1% of the cumulative heat release has occurred from the Start Of Injection (SOI). Both PRF and TPRF surrogates are considered for the current model and compared with that of Liu's model and Wang's model. It was found that the current model predicts ignition delay times closer to the experimental values compared to other models. When different surrogates are considered, TPRF surrogate predicts better compared with the PRF surrogate. This shows that the TPRF surrogate of the current model is performing well under heavy-duty engine conditions.

Figure 39 shows the comparisons between experimental and simulated Flame Lift-Off Length (FLOL) under the ambient temperature of 1100 K, the ambient pressure of 6 MPa and injection pressure of 150 MPa. The OH profiles are time averaged from 2 to 5 ms after the start of injection when combustion has stabilized. The OH boundaries are defined as 2% of the maximum OH mass fraction as per Engine Combustion Network (ECN) guidelines [73]. The simulated FLOL is defined as the distance from the injector nozzle to the first appearance of OH which forms a continuous OH profile. It can be seen that the experimental and simulated FLOL by both PRF and TPRF surrogates of the current model are very similar. FLOL is predominantly governed by the chemistry of fuel under high ambient temperatures and densities [74]. This shows that the current model is good enough to simulate HSRN combustion under diesel engine conditions.

Figure 37. IDTs validation of both HSRN and PRF60 oxidation at $\phi = 1.0$ and $p = 60 \text{ atm}$, using both PRF and TPRF surrogates.

Figure 38. IDTs validation of HSRN at ambient pressure of 60 bar, using both PRF and TPRF surrogates through 3D CFD simulations.

Figure 39. Flame lift of length validation of HSRN at ambient pressure of 60 bar using both PRF and TPRF surrogates through 3D CFD simulation.

3.6. Engine related CFD simulations

The accuracy of the presented reduced chemical kinetic model was further examined against engine experimental data. Closed-cycle simulations were performed here. The base mesh size used in this work was 4 mm. The mesh was refined to 2 mm in a geometrical cylinder that contains the cylinder region. The cylinder region had additional embedding levels with the base grid size of 1mm. The mesh near the nozzle exit was further refined to 0.25mm when during the injection process. In addition to

these fixed embedding refinements, temperature and velocity AMR with an embedding level of 3 for each were implemented, resulting in the smallest grid size of 0.25 mm in the domain. This proved to produce grid independent solution for the simulated motored runs and hence the same mesh is utilized for the subsequent GCI cases. Similar grid was utilized by our group in recent works [43, 44, 75-77]. The current reduced TPRFE chemical kinetic models was used in this work. The prediction of NO_x emissions was performed using the extended Zedovich thermal NO_x model. The soot formation and oxidation were simulated through the two-step Hiroyasu-NSC (Nagle and Strickland-Constable) approach. Acetylene was considered as the inception species in the soot model.

This particular gasoline fuel was recently investigated by our group [14]. The ignition delay times of the gasoline fuel and its surrogates were measured using shock tubes and rapid compression machines. Three surrogates were developed for the RON91 gasoline. The first was ternary Toluene Primary Reference Fuel (TPRF), the second was quaternary TPRF plus ethanol (TPRFE) and the third was an eight-component surrogate. It was shown that the TPRFE successfully predicts the ignition delay times of the real gasoline at a wide range of conditions. As such, a TPRFE surrogate was formulated following the procedure in [78], yielding a mixture with 20 vol.% n-heptane, 44.3 vol.% iso-octane, 27.5 vol.% toluene and 8.2 vol.% ethanol. The RON and MON of the TPRFE surrogate match those of the real fuel. In addition, the lower heating value of the TPRFE surrogate was changed to match the gasoline fuel and hence the same experimental fuel mass was used in the simulations.

The boundary and initial conditions listed in Table 3 are used in the engine simulations. For the closed-cycle simulations, the initial conditions at intake valve closing (IVC) were obtained from open-cycle 3-D engine simulations. The measured (average of 300 cycles) and calculated in-cylinder pressure and heat release rate (HRR) profiles are presented in Figure 40. As can be seen from Figure 40, the onset of ignition is well captured by the current model but the peak pressure is under predicted. This is partly due to the fact that the experimental pressure profile is the average of 300 cycles. However, the agreement between the measured and calculated combustion phasing is very promising considering the difficulty in resolving the chemical kinetics leading to ignition at these engine

operating conditions. The onset and magnitude of the heat release rate are also successfully predicted using the current model where low-temperature heat release prior to main combustion is observed from the calculations. This low-temperature heat release needs to be resolved correctly in order to successfully capture the ignition process which occurs at temperatures between 950 K to 1000 K at these engine conditions (not shown here).

Figure 40. Measured and calculated in-cylinder pressures and temperatures.

4. Conclusions

This work presented a new reduced kinetic mechanism for four-component (toluene/n-heptane/iso-octane/ethanol) gasoline surrogate fuels for efficient CFD applications. Stiffness analysis were performed using the computational singular perturbation (CSP) approach, and the results were compared to three literature models, demonstrating the successful stiffness removal of the mechanism. Sensitivity, rate of production (ROP) and flux analyses were also performed to demonstrate accurate predictability with such a highly reduced mechanism.

The mechanism was validated against wide range of IDT and FS data based on comprehensive literature reviews. Overall, good agreements were observed across the entire RON, equivalence ratio,

pressure and temperature range. Specifically, the proposed model was found to have better performance on IDT validation compared with Wang's model, and on FS validation compared with Liu's model.

In addition, the mechanism was coupled with the computational fluid dynamic (CFD) models to simulate the experimental data of constant volume reacting spray of a low-octane gasoline (Haltermann straight-run naphtha), and in-cylinder pressures and temperatures of a high-octane gasoline (Haltermann gasoline) combustion in a heavy-duty compression ignition engine. The combined mechanism was shown to qualitatively predict the experimentally obtained data with an improved performance for PRF, TPRF, and TPRFE surrogate. A further improved multi-component surrogate model will be developed in future work.

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