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# Development of a New Skeletal Chemical Kinetic Model of Toluene Reference Fuel with Application to Gasoline Surrogate Fuels for Computational Fluid Dynamics Engine Simulation

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## S Supporting Information

**ABSTRACT:** On the basis of our recent experience in developing a skeletal chemical kinetic model of primary reference fuel (PRF) with a semi-decoupling methodology, a new general and compact skeletal model of toluene reference fuels (TRF) consisting of 56 species and 168 reactions is presented for the oxidation of gasoline surrogate fuels. The skeletal submodel of toluene is added to the PRF model using reaction paths and sensitivity analysis. An improvement has been made in comparison to the existing skeletal models of TRF on laminar flame speed and important species evolution, while predictions of precise ignition delay are maintained. The skeletal model in this work is validated by comparison to the experimental data in a shock tube, jet-stirred reactor, flow reactor, and premixed laminar flame speed, as well as an internal combustion engine over extensive ranges of equivalence ratio, temperature, and pressure for each single fuel component and their blends. The new skeletal model is also tested using two ternary surrogates with different compositions on shock tube, laminar flame speed, and internal combustion engine. The results indicate that the overall satisfactory agreements between the predictions and experimental data are achieved.

## 1. INTRODUCTION

Real fuels usually consist of thousands of hydrocarbon components, including alkanes, olefins, and aromatics. It has been widely accepted that the oxidation characteristics of the real fuel can be properly represented by the surrogate model with a small number of components.<sup>1</sup> In the past decade, important progress has been made to represent the kinetic characteristics of real gasoline by a single component or simple mixtures of components, such as isooctane and primary reference fuel (PRF). However, some of their physical and chemical characteristics are different from real gasoline.<sup>2</sup> In recent years, with the consensus that three indispensable components in any gasoline surrogate should be *n*-heptane, isooctane, and toluene,<sup>3</sup> the chemical kinetic model of toluene reference fuel (TRF) is currently under widespread investigation. Although these surrogates contain a small number of components, it is still unfeasible to apply a detailed chemical kinetic mechanism of surrogate fuels directly to three-dimensional (3D) computational fluid dynamics (CFD) calculations because of the high cost of computational resource and time. Therefore, it is necessary to develop a skeletal model with a suitable size while maintaining sufficient performance describing combustion characteristics.

Recently, some skeletal and semi-detailed chemical kinetic mechanisms of gasoline surrogates have been developed specifically for CFD computation.<sup>4–7</sup> Mehl et al.<sup>4</sup> identified a four-component surrogate containing *n*-heptane, isooctane, toluene, and 2-pentene to represent a real gasoline. The mechanism (256 species) is reduced from a detailed kinetic mechanism of Lawrence Livermore National Laboratory (LLNL) by maintaining its performance on ignition delay times. Andrea et al.<sup>5</sup> presented a semi-detailed mechanism of TRF involving 137 species and validated it against the measured laminar flame speed under atmosphere pressure

and ignition delay in a shock tube, rapid compression machine, and homogeneous charge compression ignition (HCCI) engine. Machrafi et al.<sup>6</sup> presented an autoignition investigation concerning the TRF fuel (49 species and 83 reactions) in a HCCI engine. Kim et al.<sup>7</sup> developed a reduced TRF mechanism with 44 species for gasoline surrogate by validating the measurements in a shock tube and rapid compression machine. It seems that the semi-detailed mechanisms developed using reliable algorithms,<sup>8,9</sup> such as those of Mehl et al. and Andrea et al., still cost too much computer time in CFD computation, because a relatively great number of species (usually more than 100) is contained and it will reach the limit of the method for further reduction.<sup>10</sup> On the other hand, some skeletal models may lose some important combustion characteristics, such as flame propagation in a spark-ignition (SI) engine and important species evolution,<sup>11,12</sup> because the reduction process was globally conducted on the reactions involving both small and large molecules over the entire temperature range, which might destroy the highly integrated characteristics in the chemical mechanism. In this view, the basic objective of this paper is to construct a skeletal model of TRF with the application on gasoline surrogate fuel in 3D CFD simulation, by retaining the number of species as small as possible while preserving its good performance in different reactors and under extensive operating conditions.

It should be also noted that, although Kukkadapu et al.<sup>13</sup> have investigated the surrogate models for the gasoline with non-oxygenated components and found that the four-component surrogate (TRF + 2-pentene) emulated the more accurate ignition delay times of gasoline, TRF has been widely employed in gasoline surrogates in both theoretical and

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experimental work, while the four-component surrogate is not the ultimate model and more components could be involved.<sup>4,13</sup> Moreover, the TRF skeletal model developed in this study is an extension of our previous PRF model using a semi-decoupling methodology.<sup>12</sup> On the basis of the good accomplishment achieved in this study, future work by adding more components to TRF will be performed to improve the overall performance of gasoline surrogate.

In the following, a submodel of toluene is integrated into the skeletal PRF model that we developed lately<sup>12</sup> and, consequently, a skeletal model of TRF, including 56 species and 168 reactions, for describing the oxidation and combustion characteristics of the gasoline surrogate fuel is constructed. The new skeletal mechanism is widely validated against the experimental measurements in different reactors under extensive operating conditions, with special focuses on the laminar flame speed, major species evolution (such as fuel, CO, CO<sub>2</sub>, etc.), and exhaust gas recirculation (EGR) conditions.

## 2. CONSTRUCTION OF THE SKELETAL MODEL

It is apparent that, the more experiments are validated, the more reliable a chemical kinetic mechanism is. Therefore, in this paper, we validate the new skeletal model in various reactors, especially for laminar flame speed and some critical species evolution, which have not been sufficiently examined in some previous skeletal models. On the basis of the theory conclusion and observation of You et al.<sup>14</sup> and Ranzi et al.,<sup>15</sup> we achieved these targets successfully using a semi-decoupling methodology in our previous work of developing a skeletal PRF model.<sup>12</sup> This methodology treats the alkane oxidation as two parts: one is flame propagating after ignition, which is represented by a detailed and comprehensive 'core' mechanism of C0–C1, and the other is a skeletal model that is coupled with the 'core' to describe ignition characteristic. Unlike the method using global reduction, this methodology only reduces large molecule mechanisms while keeping a mechanism of small hydrocarbons as its previous form, because these species are almost indispensable. Thereby, the number of species in the final model developed using this methodology can be sufficiently reduced, while the essential combustion information (such as important species concentrations and laminar flame speed) can be satisfactorily predicted. Moreover, during the construction of a skeletal model for fuel blends based on this practical methodology, only the large molecule subset of the corresponding fuel is needed to be developed for the control of the ignition characteristics, instead of a complicated reconstruction of the entire mechanism.

However, the construction of a skeletal model for toluene, which is suitable for various applications, is considerably more difficult than that for PRF using this methodology. This is attributed to two reasons. First, toluene is an aromatic hydrocarbon whose molecular structure is different from that of alkane. This difference causes more complicated and diverse reaction paths, which involve more species and elementary reactions. Second, toluene does not have the negative temperature coefficient (NTC) effect and ignites only in a relatively high temperature range (higher than 1000 K). Therefore, the high-temperature submodel for toluene oxidation has a much greater influence on the ignition delay time and laminar flame speed compared to the case of alkane. Moreover, even for existing comprehensive and detailed mechanisms of toluene, the predictions still show some differences against experimental data.<sup>16</sup> Hence, considering the compact size of the skeletal model, at this stage, we can only pay attention to some of the important and concerned engine combustion characteristics (such as laminar flame speed and important species evolution under relatively high pressure).

The idea of constructing a toluene mechanism is similar to the semi-decoupling methodology: combining a skeletal frame of large-molecule reactions with a comprehensive 'core' mechanism of C0–C1. First of all, to reproduce the main combustion process of toluene, a series of reaction paths of toluene used in different chemical kinetic

mechanisms for various reactors<sup>17–20</sup> is considered and an analysis of the reaction paths and sensitivity is performed. On this basis and in view of keeping a small size of the skeletal model, the reaction path shown in Figure 1 is chosen in this work.

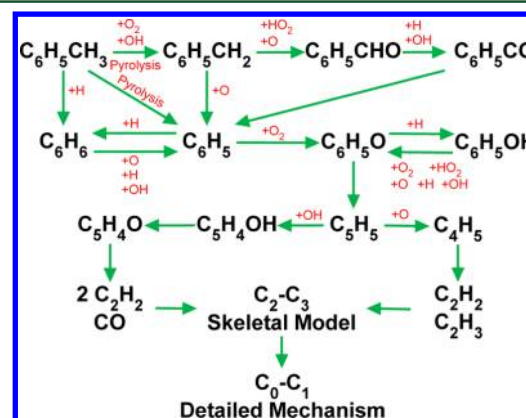


Table 1. Reactions of the Toluene Branch<sup>a</sup>

reactions ( $k = AT^{**}b \exp(-E/RT)$ )	A	b	E	reference
Toluene Reaction Branch				
25. $C_6H_5CH_3 = C_6H_5CH_2 + H$	$2.09 \times 10^{15}$	0.0	87463.4	21
26. $C_6H_5CH_3 = C_6H_5 + CH_3$	$2.66 \times 10^{16}$	0.0	97830.4	21
27. $C_6H_5CH_3 + O_2 = C_6H_5CH_2 + HO_2$	$1.50 \times 10^{14}$	0.0	41400.0	22
28. $C_6H_5CH_3 + H = C_6H_5 + CH_3$	$1.20 \times 10^{13}$	0.0	5100.0	22
29. $C_6H_5CH_3 + OH = C_6H_5CH_2 + H_2O$	$3.00 \times 10^{12}$	0.0	1700.0	22
30. $C_6H_5CH_2 + O = C_6H_5CHO + H$	$2.11 \times 10^{14}$	0.0	0.0	21
31. $C_6H_5CH_2 + O = C_6H_5 + CH_2O$	$1.19 \times 10^{14}$	0.0	0.0	21
32. $C_6H_5CH_2 + HO_2 \Rightarrow C_6H_5CHO + H + OH$	$5.00 \times 10^{14}$	0.0	0.0	this work
33. $C_6H_5CHO + OH = H_2O + C_6H_5CO$	$3.44 \times 10^9$	1.2	-447.0	21
34. $C_6H_5CHO + H = H_2 + C_6H_5CO$	$2.28 \times 10^{10}$	1.1	3279.0	21
35. $C_6H_5CO = C_6H_5 + CO$	$3.00 \times 10^{12}$	0.0	34860.0	21
36. $C_6H_6 + H = C_6H_5 + H_2$	$2.00 \times 10^{13}$	0.0	18600.0	21
37. $C_6H_6 + OH = C_6H_5 + H_2O$	$1.63 \times 10^8$	1.4	1451.0	21
38. $C_6H_6 + O = C_6H_5 + OH$	$2.00 \times 10^{13}$	0.0	14700.0	21
39. $C_6H_5 + H = C_6H_6$	$2.00 \times 10^{14}$	0.0	0.0	5
40. $C_6H_5 + O_2 = C_6H_5O + O$	$2.60 \times 10^{13}$	0.0	6100.0	5
41. $C_6H_5O = C_5H_5 + CO$	$7.40 \times 10^{11}$	0.0	43900.0	21
42. $C_6H_5O + H = C_6H_5OH$	$2.50 \times 10^{14}$	0.0	0.0	21
43. $C_6H_5OH + O_2 = C_6H_5O + HO_2$	$1.00 \times 10^{13}$	0.0	38000.0	21
44. $C_6H_5OH + H = C_6H_5O + H_2$	$1.20 \times 10^{14}$	0.0	12400.0	21
45. $C_6H_5OH + O = C_6H_5O + OH$	$1.30 \times 10^{13}$	0.0	2900.0	21
46. $C_6H_5OH + OH = C_6H_5O + H_2O$	$3.00 \times 10^6$	2.0	-1310.0	21
47. $C_6H_5OH + HO_2 = C_6H_5O + H_2O_2$	$1.00 \times 10^{12}$	0.0	1000.0	21
48. $C_5H_5 + O = C_4H_5 + CO$	$3.20 \times 10^{13}$	-0.2	440.0	5
49. $C_5H_5 + OH = C_5H_4OH + H$	$3.50 \times 10^{57}$	-12.2	48350.0	5
50. $C_5H_4OH = C_5H_4O + H$	$2.10 \times 10^{13}$	0.0	54000.0	5
51. $C_5H_4O \Rightarrow C_2H_2 + C_2H_2 + CO$	$5.70 \times 10^{32}$	-6.8	68500.0	5
52. $C_5H_4O \Rightarrow C_2H_2 + C_2H_2 + CO$	$6.20 \times 10^{41}$	-7.9	98700.0	5
53. $C_4H_5 = C_2H_2 + C_2H_3$	$1.00 \times 10^{14}$	0.0	43890.0	21

<sup>a</sup>A units are mol cm s K, and E units are cal/mol.

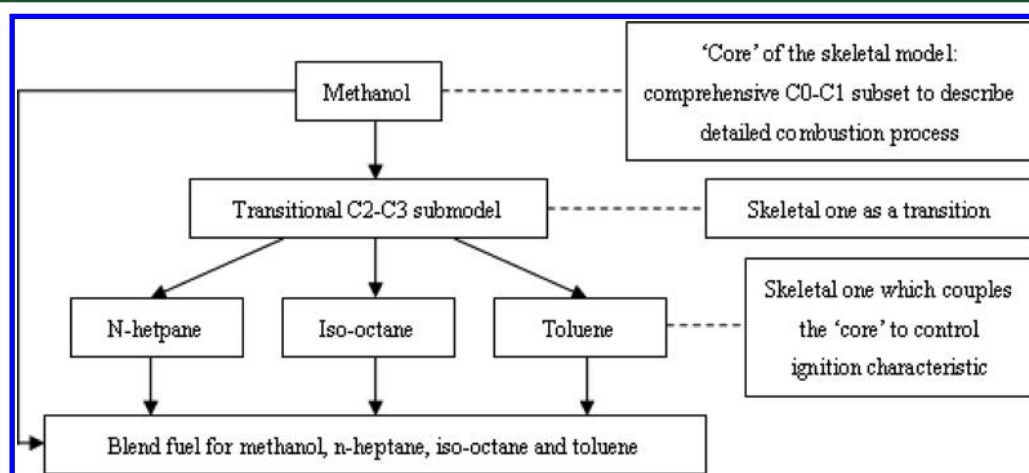


Figure 2. Schematic diagram of the skeletal model structure.

of toluene/air for equivalence ratios of 0.25, 0.5, and 1.0. To assess the capacity of our skeletal model, the calculated ignition delay times by the mechanisms of Andrae et al.<sup>5</sup> and Mehl et al.<sup>4</sup> are also presented in the figures. Overall, it can be seen that the ignition delay times calculated by the new skeletal model show good agreement with the experimental data under a higher pressure of 5.0 MPa for various equivalence ratios, while little differences are found for the lower pressure of 1.2 MPa. Meanwhile, all of the mechanisms fail to exactly predict the ignition delay time at the lower pressure of 1.2 MPa. At a

higher pressure of 5.0 MPa, the agreements between predicted and measured results are generally improved in comparison to the case of 1.2 MPa. As mentioned above, because the existing detailed mechanisms of TRF fail to predict experimental data precisely, the development of a well-performed skeletal model based on these detailed mechanisms would be a difficult task.

**3.1.2. Jet-Stirred Reactor.** Model validation of important species concentrations (toluene, CO, and CO<sub>2</sub>) in a jet-stirred reactor was performed against experimental data from Moréac et al.<sup>28</sup> The temperature range is from 550 to 1180 K; the



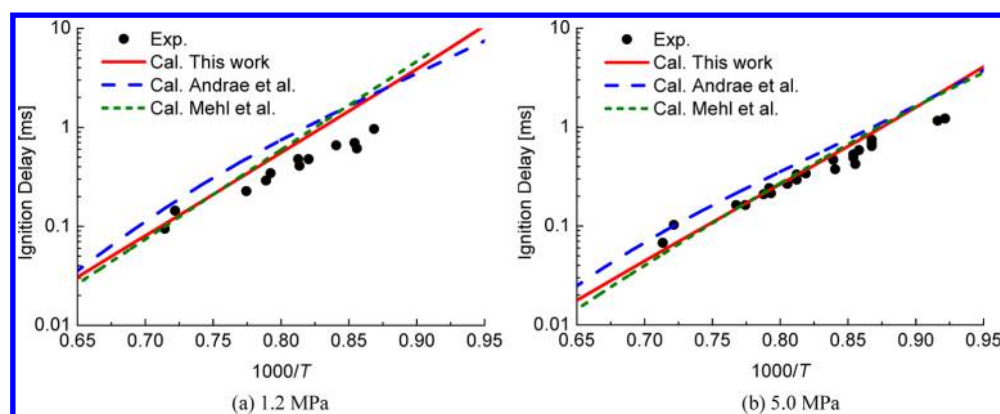


Figure 3. Comparison of some detailed mechanisms to our skeletal model in a shock tube.  $\phi = 0.25$ .

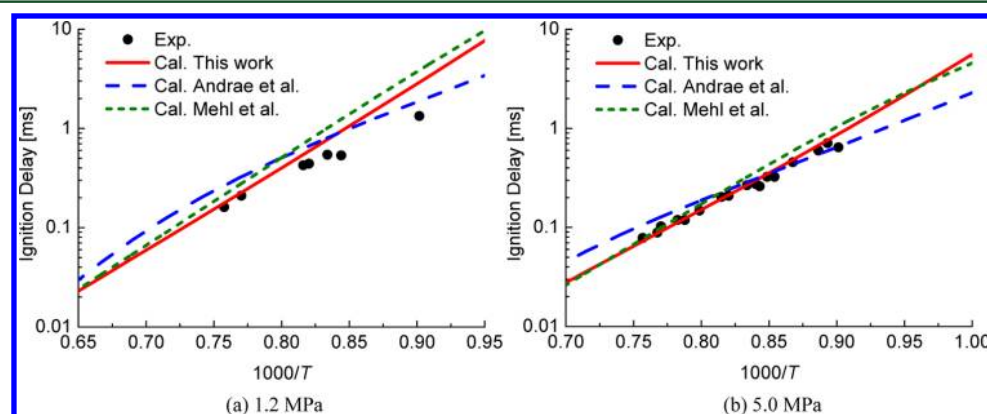


Figure 4. Comparison of some detailed mechanisms to our skeletal model in a shock tube.  $\phi = 0.5$ .

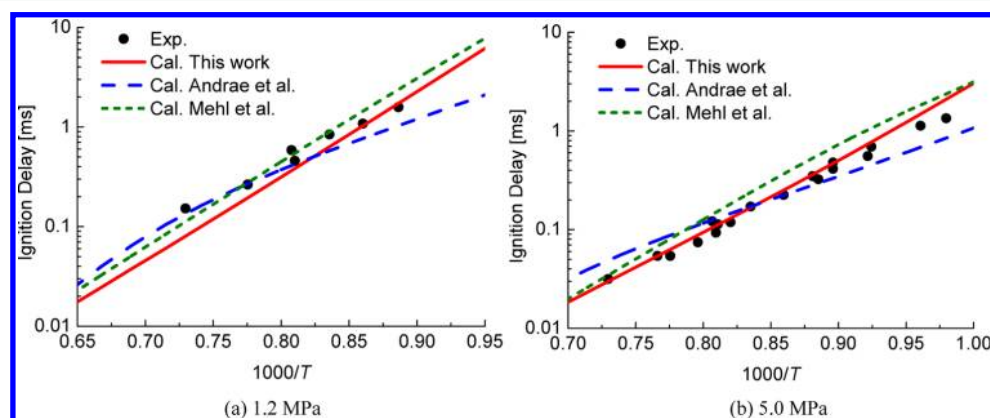


Figure 5. Comparison of some detailed mechanisms to our skeletal model in a shock tube.  $\phi = 1.0$ .

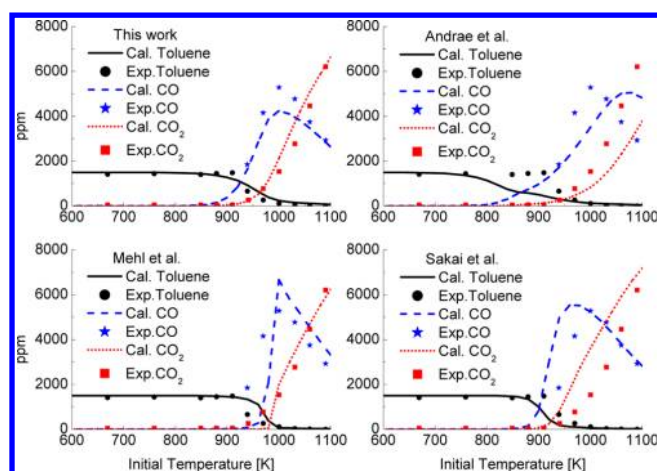
pressure is 1.0 MPa; the equivalence ratio is 1.0 with highly diluted nitrogen; and the residence time is 1.0 s. The results computed by the mechanisms from Andrae et al.,<sup>5</sup> Mehl et al.,<sup>4</sup> and Sakai et al.<sup>21</sup> are also illustrated for comparison, as shown in Figure 6. It can be seen that the evolutions of toluene, CO, and CO<sub>2</sub> predicted by our skeletal model match the experimental data well, except that the peak value of CO at 1000 K is underpredicted. Our results seem even better than those by the models of Andrae et al.<sup>5</sup> and Sakai et al.<sup>21</sup>

**3.1.3. Flow Reactor.** Experiments in a variable pressure flow reactor (VPFR) were performed by Chaos et al.<sup>2</sup> Figure 7 shows temporal evolutions of CO, CO<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub>, and toluene mole fractions during toluene oxidation under the conditions:  $P = 1.25$  MPa,  $T = 920$  K,  $\phi = 0.6$ , and initial toluene mole

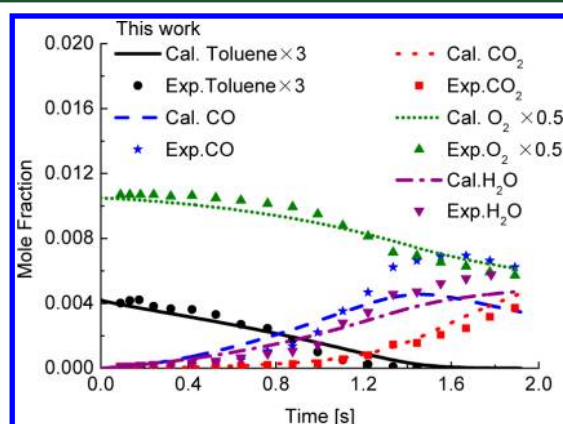
fraction = 0.14%. It can be seen that the calculated mole fractions of toluene, CO<sub>2</sub>, and O<sub>2</sub> are close to the experimental data, while the result for CO is not satisfactory. A similar phenomenon is found in ref 2.

Figure 8 shows the sum of CO and CO<sub>2</sub> mole fractions for toluene oxidation at a fixed residence time compared to experiments as well as predictions by three semi-detailed models by Andrae et al.,<sup>5</sup> Mehl et al.,<sup>4</sup> and Sakai et al.<sup>21</sup> It is clear that the combined CO and CO<sub>2</sub> mole fractions computed by our model agree well with the experimental data and are close to the results by Mehl et al.<sup>4</sup> and Sakai et al.,<sup>21</sup> which are better than the prediction by Andrae et al.<sup>5</sup>

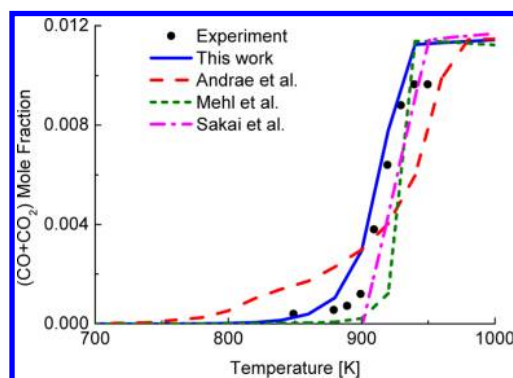
**3.1.4. Laminar Flame Speed.** Using the counterflow twin-flame technique, Davis et al.<sup>20</sup> measured the toluene/air laminar



**Figure 6.** Comparison of experimental<sup>28</sup> and modeling results for species concentrations in a jet-stirred reactor.  $P_1 = 1$  MPa, and residual time is 1 s, with 0.15% toluene and 1.35%  $O_2$ .

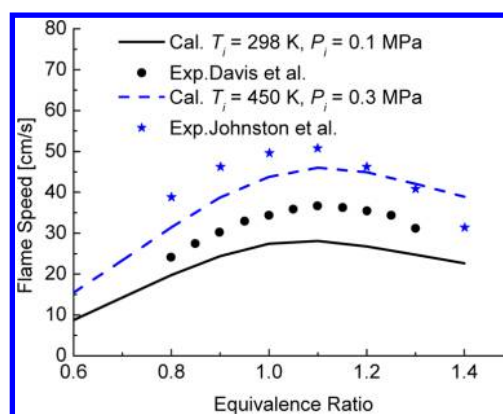


**Figure 7.** Comparison of experimental<sup>2</sup> and modeling results of toluene oxidation in a flow reactor.  $P = 1.25$  MPa,  $T = 920$  K,  $\phi = 0.6$ , and  $X_{\text{toluene}} = 0.14\%$ .



**Figure 8.** Comparison of experimental<sup>2</sup> and modeling results of toluene oxidation in flow reactor conditions of  $P = 1.25$  MPa,  $\phi = 1.0$ ,  $X_{O_2} = 0.015$ , and residence time = 1.8 s.

flame speeds. The temperature is 298 K; the pressure is 0.1 MPa; and the equivalence ratio is 0.8–1.4. Johnston and Farrell<sup>29</sup> presented laminar flame speeds for toluene/air in a combustion chamber. The temperature is 450 K; the pressure is 0.3 MPa; and the equivalence ratio is 0.8–1.3. Figure 9 shows the comparison of the modeling results to the two experiments. It can be seen that most predicted laminar flame speeds are



**Figure 9.** Comparison of experimental<sup>20,29</sup> and modeling laminar flame speeds of toluene/air.

lower than experimental data by about 20%. As mentioned above, toluene is an aromatic hydrocarbon that has a complex molecular structure and reaction process. To keep the skeletal model compact, many unimportant reaction paths and species affecting the ignition delay time are eliminated, although they might have a certain influence on the laminar flame speed. This is why there is a discrepancy between predictions and experimental data. Although this problem is not the major issue concerned in this study, because these results are obtained under quite low pressures, which are not the engine-relevant conditions, this indicates that our model is still incomplete in the context of laminar flame speed and further studies and improvements are needed. Validations of laminar flame speed under relatively high pressures are discussed in section 3.2.2.

### 3.2. Toluene Reference Fuel and Gasoline Surrogates.

In this section, validations of the new skeletal model of TRF with application on gasoline surrogate fuels are carried out by comparisons to the detailed mechanism from LLNL.<sup>4</sup> Components of gasoline surrogates selected and tested are shown in Table 2.

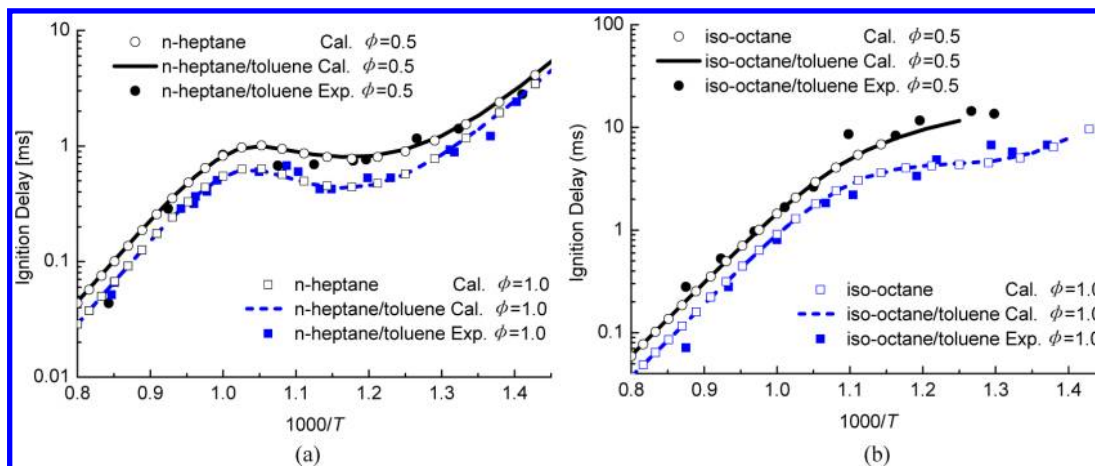
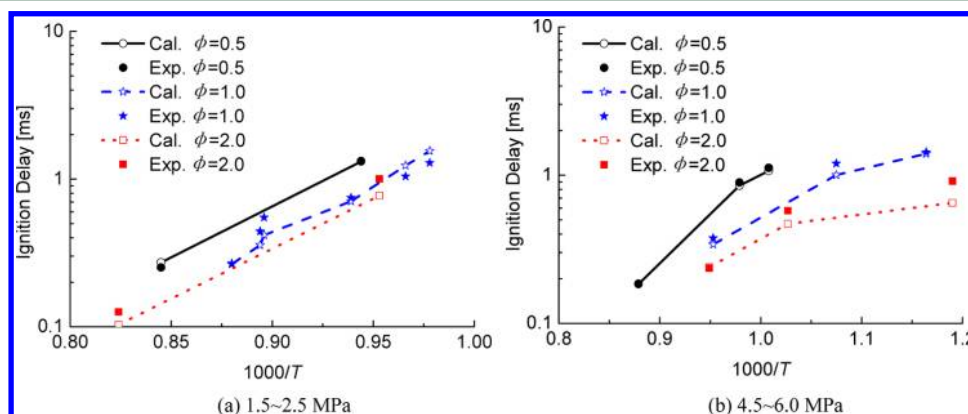
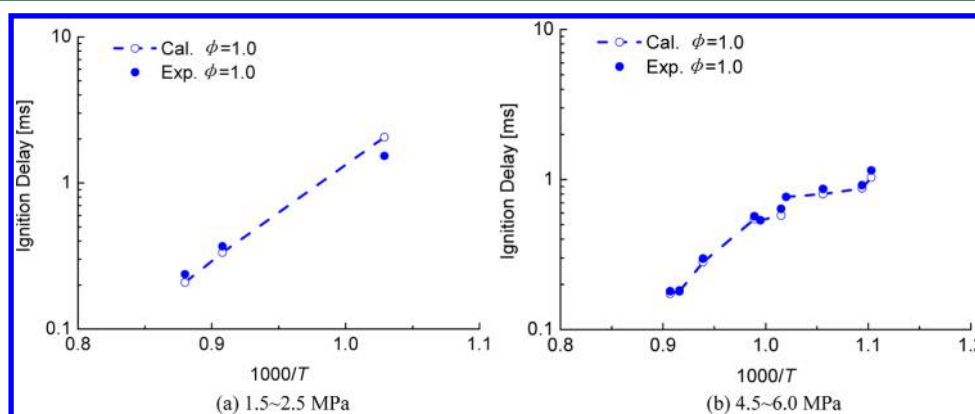
**3.2.1. Shock Tube.** Hartmann et al.<sup>31</sup> investigated the effect of toluene experimentally on the ignition delay times of *n*-heptane/air and isooctane/air under 4.0 MPa in a shock tube. The experiments were carried out on *n*-heptane/toluene (90:10, vol %) and isooctane/toluene (90:10, vol %) at  $\phi = 0.5$  and 1.0 and in a temperature range from 700 to 1200 K. They found from the experiment and simulation that adding a small amount of toluene (<10 vol %) has little influence on the autoignition for *n*-heptane and isooctane. Figure 10 shows comparisons of ignition delay times simulated by our new model to the measured data from ref 31 for *n*-heptane/toluene (90:10, vol %) and isooctane/toluene (90:10, vol %) in air. The results show that the computed ignition delay times match the experimental data well. It is also important to note that the simulation results verify the above conclusion in ref 31.

Gauthier et al.<sup>30</sup> studied autoignition characteristics of TRF/air and gasoline/air mixtures with and without EGR in a shock tube under engine-relevant conditions. They suggested two surrogates comprised of isooctane, toluene, and *n*-heptane with the proportions of surrogate A (63:20:17, vol %) and surrogate B (69:14:17, vol %) or surrogate A (56:28:17, mol %) and surrogate B (63:20:17, mol %).

Figures 11 and 12 show comparisons of experimental and calculated ignition delay times of surrogates A and B without EGR in the pressure ranges of 1.5–2.5 and 4.5–6.0 MPa, respectively. The results show that the ignition delay times

Table 2. Components of Gasoline Surrogate Fuel

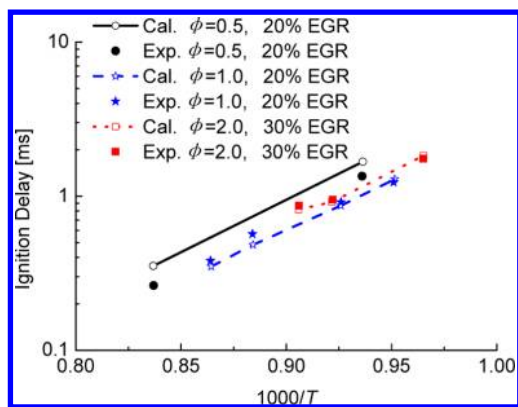
	RON	MON	H/C	components (mole fraction)				reference
				isooctane (%)	toluene (%)	<i>n</i> -heptane (%)	2-pentene (%)	
surrogate A	88.0	85.0	1.971	56	28	17	0	30
surrogate B	87.0	85.0	2.052	63	20	17	0	30
Mehl et al.	91	83	1.925	48.8	30.6	15.3	5.3	4

Figure 10. Comparison of experimental<sup>31</sup> and modeling ignition delay times in a shock tube.  $P = 4.0$  MPa.Figure 11. Comparison of experimental<sup>30</sup> and simulated ignition delay times of surrogate A in a shock tube.Figure 12. Comparison of experimental<sup>30</sup> and simulated ignition delay times of surrogate B in a shock tube.

computed by our model match the experimental data well in the two pressure ranges for both surrogates A and B. Both the variation trend and values predicted by this work are very close to the experiments.

Figure 13 shows comparisons of experimental and calculated ignition delay times of surrogate A with EGR under pressures of 1.5–2.5 MPa. The results show that the ignition delay times computed by our model still exhibit a very good agreement





**Figure 13.** Comparison of experimental<sup>30</sup> and simulated ignition delay times of surrogate A in a shock tube under pressures of 1.5–2.5 MPa.

with the experimental data, although the predictions for the case of 0.5 equivalence ratio and 20% EGR are a little higher than experiments.

To test the skeletal TRF model applied to gasoline surrogate fuels, validations on gasoline (RD387) ignition without EGR (experimental data are from Gauthier et al.<sup>30</sup>) compared to the mechanism of Mehl et al.<sup>4</sup> are shown in Figures 14 and 15. In general, the predictions of both the skeletal model and detailed mechanism perform well, except for some certain data points. Surrogates A and B have very close predicted values. The discrepancies between experiment and simulation and between the two models may be due to the difference in the surrogate formulation.

Figure 16 presents the comparisons of experimental and calculated ignition delay times of this work and the work of Mehl et al.<sup>4</sup> with EGR. The results show that our skeletal model exhibits a good agreement with the experimental data, whereas the mechanism of Mehl et al. provides a little higher prediction. Surrogates A and B still have close predicted values in a shock tube with EGR.

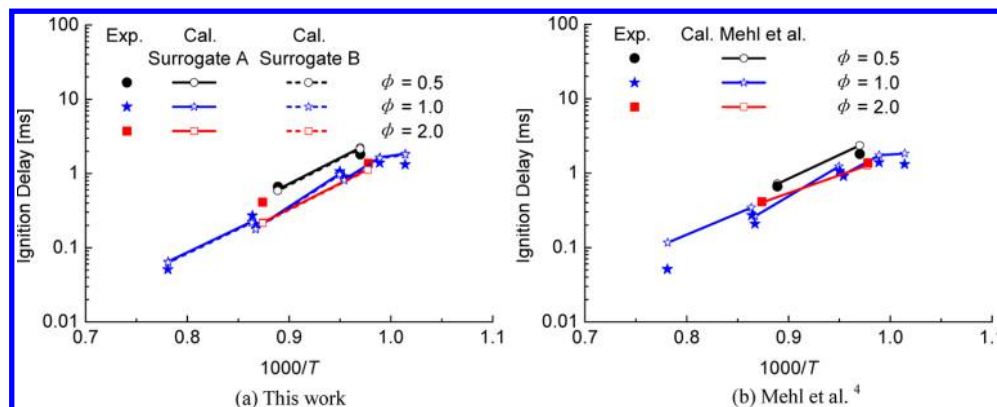
**3.2.2. Laminar Flame Speed.** Zhao et al.<sup>32</sup> determined the laminar flame speed for mixtures of unleaded conventional gasoline (CR-87, octane number = 87) and air by employing a stagnation jet-wall flame device and particle image velocimetry (PIV). The temperatures are 353 and 500 K; the pressure is 0.1 MPa; and the equivalence ratio is 0.7–1.3. Nitrogen dilution effects were also studied for the same conditions. The laminar flame speed was obtained using linear extrapolation of stretched flame data to zero stretch rate. Figures 17 and 18 show

comparisons of the experimental and calculated laminar flame speeds for the gasoline/air mixture and with N<sub>2</sub> dilution, respectively. The results show that the predictions of our skeletal model match the experimental data well. The two gasoline surrogate fuels have nearly the same laminar flame speed values calculated by our skeletal model under these operating conditions.

As revealed in Figure 18, flame propagation is clearly affected by dilution with inert or exhaust gases. Therefore, it is important to validate the dilution effects on the laminar flame speed for practical fuels. Jerzembeck et al.<sup>33</sup> measured the laminar flame speed of the gasoline (octane number = 90) and air mixture in a constant volume vessel. The initial temperature is 373 K; the pressures are 1.0–2.5 MPa; and the equivalence ratios are 0.7–1.2. Nitrogen dilution effects were also studied for the same conditions. Figures 19 and 20 show the comparisons between measured and calculated laminar flame speeds for the gasoline/air mixture and with N<sub>2</sub> dilution, respectively. Results by the detailed mechanism of Mehl et al.<sup>4</sup> are also compared. It can be seen that the results obtained from our new skeletal model are in reasonably good agreement with the experimental data at high pressures, except for the dilution condition at a lower pressure of 1.0 MPa. Surrogates A and B have nearly identical predicted values.

It can be seen from Figure 19 that our skeletal model illustrates even better performance than the reduced mechanism by Mehl et al.<sup>4</sup> However, this might not be true in reality. First, the composition of the surrogate used by Mehl et al. is different from those in our simulations. Second, as mentioned in ref 4, the 256 species skeletal mechanism developed by Mehl et al. did not predicted well in laminar flame speeds at high pressures because of the fact that the reduction was mainly focused on the ignition delay time without including some important reactions for flame propagation. Considering the different components of the three surrogates, although the skeletal model in this work did a better job in predicting the gasoline ignition delay time and laminar flame speed, more studies are still needed to clarify the reasons for these discrepancies. Possible factors, besides the surrogate formulation, include uncertainty in the chemical kinetic mechanism and deviations in the experiment.<sup>4</sup>

**3.2.3. Internal Combustion Engine.** Finally, the validations in a 3D CFD simulation are applied to examine the performance of the skeletal model in HCCI engines. The simulations are performed by integrating CHEMKIN III with an updated KIVA-3V code<sup>34</sup> with the improvements for several



**Figure 14.** Comparison of experimental<sup>30</sup> and simulated ignition delay times at 1.5–2.5 MPa in a shock tube.



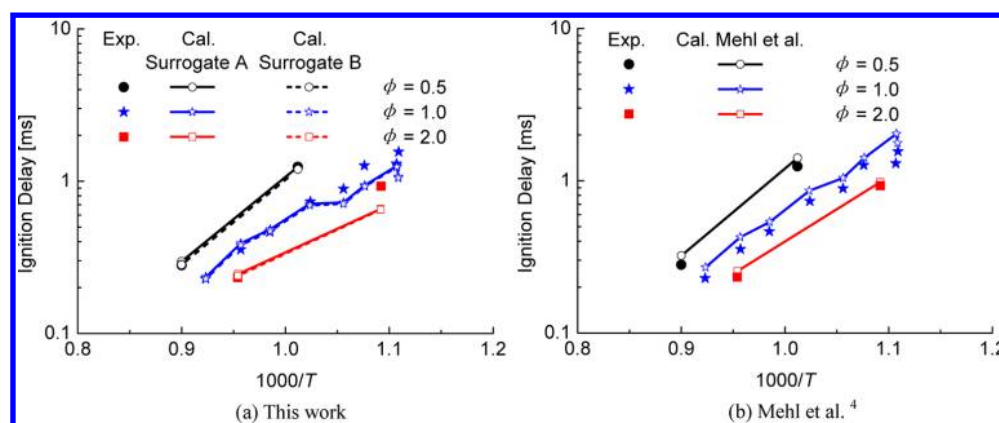


Figure 15. Comparison of experimental<sup>30</sup> and simulated ignition delay times at 4.5–6.0 MPa in a shock tube.

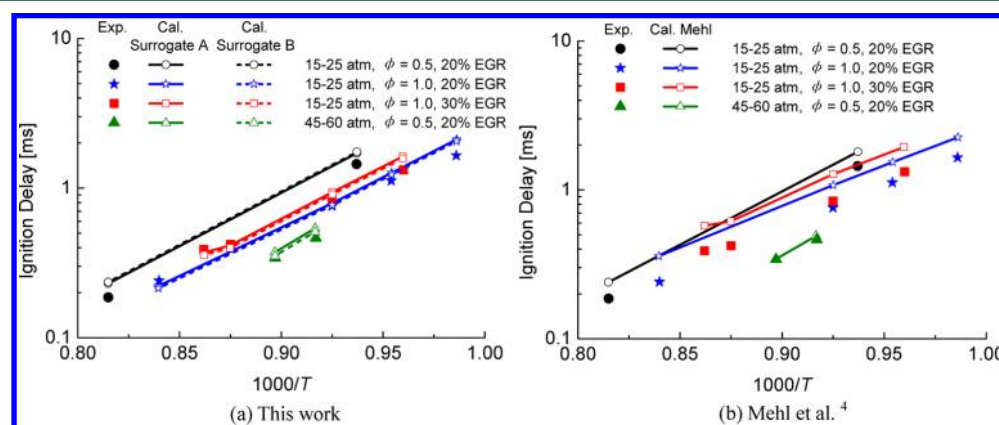


Figure 16. Comparison of experimental<sup>30</sup> and simulated ignition delay times of this work and the work of Mehl et al.<sup>4</sup> in a shock tube.

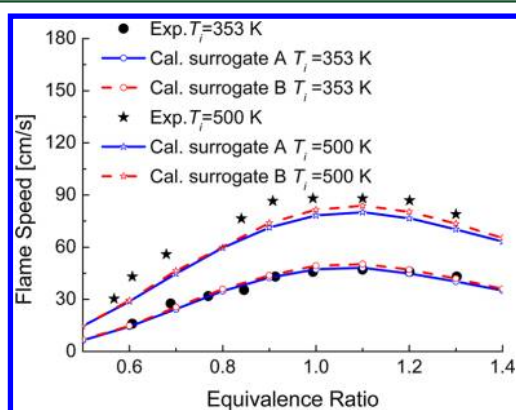


Figure 17. Comparison of experimental<sup>32</sup> and modeling laminar flame speeds for the gasoline/air mixture.

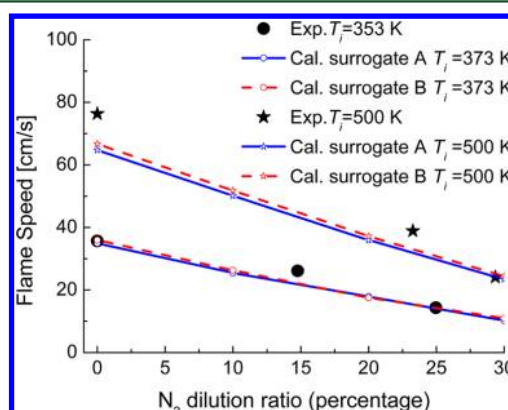
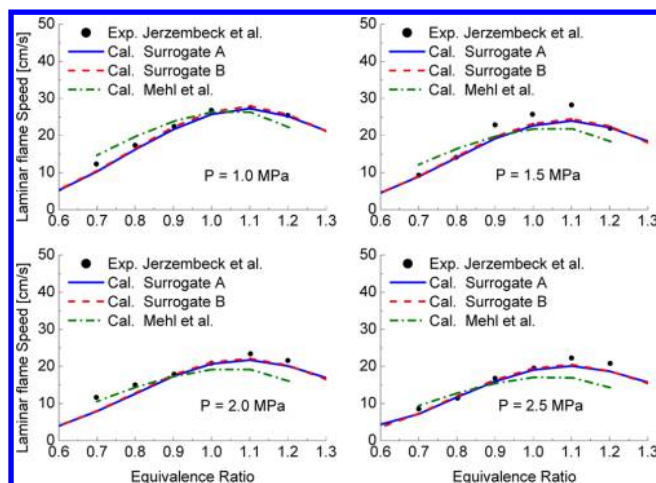


Figure 18. Comparison of experimental<sup>32</sup> and modeling laminar flame speeds for the gasoline/air mixture with N<sub>2</sub> dilution.  $\phi = 0.84$ .

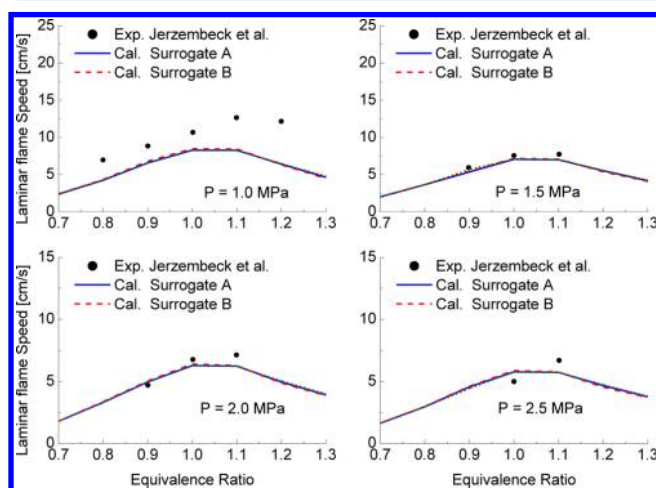
models. More introductions about the computational model can be found in our previous work.<sup>11,12</sup>

The validation experiment for a HCCI engine using gasoline as fuel is taken from Kalghatgi and Head.<sup>35</sup> The engine is a Ricardo Hydra single-cylinder research engine with a Typhon four-valve cylinder head with a pent roof. The piston has a raised piston crown required to achieve the compression ratio of 14. Bore  $\times$  stroke = 86  $\times$  86 mm. The fuel used is unleaded gasoline, ULG 95, which has a research octane number (RON) of 95.7, and motor octane number (MON) of 87.6, and (H/C)<sub>a</sub> = 1.991. Other detailed engine specifications can be found in ref 35. The computational grid consists of 93 174 cells in a 3D cylinder, as shown in Figure 21.

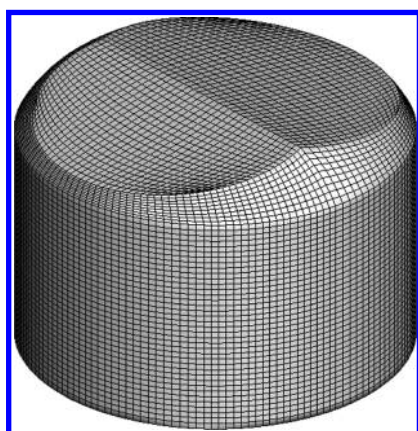
Figure 22 provides the comparison results between the predicted and measured in-cylinder pressure and heat release rate traces. It can be easily seen that the predicted in-cylinder pressure agrees well with the measurements, while the heat release rate is slightly overestimated. This is due to the fact that some uncertainties in the input parameters could be introduced in the simulations, including the estimation of the initial conditions and the simplification of the in-cylinder geometry. It should also be noted that, using this skeletal model for gasoline surrogate fuels, in this engine case, surrogate B ignites at nearly the same time as in the experiment, while surrogate A delays by about 1° CA under the same input conditions.



**Figure 19.** Comparison of experimental<sup>33</sup> and modeling laminar flame speeds for the gasoline/air mixture.

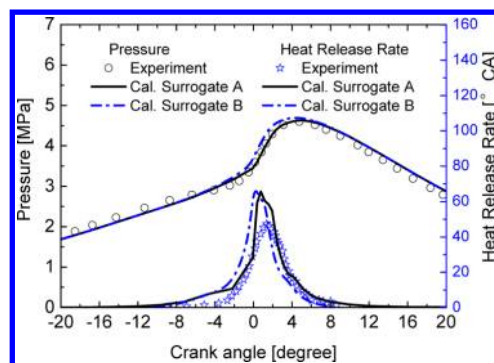


**Figure 20.** Comparison of experimental<sup>33</sup> and modeling laminar flame speeds for the gasoline/air mixture with N<sub>2</sub> dilution.  $X_{\text{air O}_2} = 0.15$ .



**Figure 21.** View of the KIVA-3V grid at 90° crank angle (CA) before top dead center (TDC).

The CFD modeling provided an amount of detailed information about the engine combustion process. Because of the space limit, here, only an example is present in Figure 23, which illustrates the simulated evolution of some important species for surrogates A and B. To display the consumption rates of *n*-heptane and isooctane clearly, the mass of *n*-heptane



**Figure 22.** Comparison of experimental<sup>35</sup> and modeling results for cylinder pressure and heat release rate history in a HCCI engine using gasoline as fuel. The equivalence ratio is 0.2857.

is multiplied by factors of 3.74 and 4.23 for surrogates A and B, respectively, to make sure that the initial mass of *n*-heptane and isooctane is equal at  $-30^\circ$  CA. It can be seen that, *n*-heptane has a higher consumption rate at the beginning (about  $-30^\circ$  CA) and an earlier quick consumption time than isooctane, while toluene reacts the latest, at nearly  $-3^\circ$  CA, when the cylinder pressure starts to rise quickly. This is apparently in coincidence with the realistic situations. CO and H<sub>2</sub>O are produced along with the *n*-heptane and isooctane consumption, while CO<sub>2</sub> rises suddenly upon the final ignition. It can also be seen that surrogates A and B exhaust nearly the same ultimate emissions of CO, CO<sub>2</sub>, and H<sub>2</sub>O. However, for HC emission, surrogate A produces 7.435 g/kg of fuel, while surrogate B produces 5.459 g/kg of fuel (not shown in the figure). These results can serve as an assessment of the two gasoline surrogates in engine applications.

#### 4. CONCLUSION

A new general and compact skeletal chemical kinetic model of TRF oxidation consisting of 56 species and 168 reactions is developed by adding a submodel of toluene into the PRF skeletal model developed in our previous work. The new skeletal model is extensively validated by comparison to the experimental measurements in different reactors under wide operating conditions. Two ternary gasoline surrogates with different compositions are tested on a shock tube, laminar flame speed, and internal combustion engine and compared to real gasoline. The predicted results show good agreement with the measurements, especially for laminar flame speed. Major findings and observations of this study can be summarized as follows: (1) Construction of a skeletal model of toluene, which is suitable for various reactors, is considerably more difficult than that of PRF using the semi-decoupling methodology proposed by the authors recently, because toluene is an aromatic hydrocarbon whose molecular structure is different from that of alkane. This difference causes more complicated and diverse reaction paths, which involve more species and elementary reactions. Furthermore, toluene does not have the NTC behavior and ignites only in a relatively high temperature range (higher than 1000 K). Therefore, the high-temperature submodel for toluene oxidation has a much greater influence on the ignition delay time and laminar flame speed compared to the case of alkane. (2) The experience and discoveries obtained throughout the research on the oxidation mechanisms of PRF and toluene indicate that the comprehensive 'core' mechanism (C0–C1) plays the fundamental and critical role in the semi-

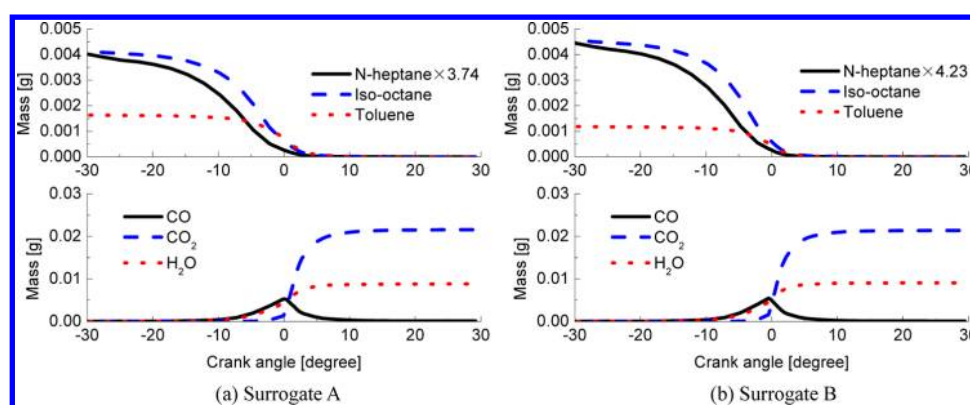


Figure 23. Simulated species evolution in an internal combustion engine for surrogates A and B.

decoupling method. With the introduction of relevant large-molecule reactions (a skeletal subset) to the 'core', skeletal models for specific fuels with various components can be constructed. As reported in this paper, the successful practice in constructing and improving the new skeletal model of TRF demonstrates again that this methodology of developing a skeletal model for multi-component fuel is effective and generally applicable. (3) The new skeletal model of TRF is tested using two ternary surrogates with different compositions on a shock tube, laminar flame speed, and internal combustion engine compared to real gasoline. The predicted results of relevant combustion parameters for surrogates A and B are very close using the skeletal model. The comparison to the semi-detailed mechanism by Mehl et al. indicates that further investigation is still necessary to clarify the reasons for some existing discrepancies between the two models. Possible factors, besides the surrogate formulation, include uncertainty in the chemical kinetic model and the accuracy of the experimental data. (4) Up to now, the TRF model has been validated mostly on fundamental experiments and only on one HCCI engine. The available experimental data on real engines are still not sufficient to validate the present skeletal model. In view of its good performance in the flame speed prediction, the current version of the model should be further validated and evaluated for gasoline direct injection (GDI) and SI engines.

## ■ ASSOCIATED CONTENT

### Supporting Information

Mechanism, thermal, and transport files of the skeletal TRF model. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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