Understanding the Blending Octane Behaviour of Unsaturated Hydrocarbons: A Case Study of C_4 Molecules and Comparison with Toluene

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Abstract

Octane number (ON) is an important empirical parameter for developing and optimizing internal combustion engine (ICE) for knock resistance. Primary reference fuels (PRF) comprising iso-octane and n-heptane are the simplest gasoline surrogates. C_4 hydrocarbons: butane isomers (n-butane and isobutane), butene isomers (1-butene, 2-butene and isobutene) and 1,3-butadiene are the smallest hydrocarbons with isomeric, saturated, unsaturated and conjugated bond structures, which makes them good candidates for understanding the blending octane behavior of saturated and unsaturated hydrocarbons. In this study, the blending octane behaviors of six PRF60 & C_4 hydrocarbon mixtures were systematically investigated. A state-of-the-art kinetic models were used by merging the latest KAUST gasoline surrogate model with the AramcoMech 3.0 model. IDTs of stoichiometric fuel/air mixtures were simulated at wide range of pressure (20 – 50 atm) and temperature (600 – 1400 K). Three correlation equations were employed from the literature to predict the research octane number (RON) and motor octane number (MON) of all blends based on these calculated IDTs. Compared with the experimentally measured ON, the best correlation conditions and errors were identified. With the highest degree of unsaturation, 1,3-butadiene was found to be the strongest ON enhancer. Moreover, based on a polynomial correlation, a TPRF (PRF + toluene) blend was formulated by matching the RON and MON of PRF plus 1,3-butadiene blend, for a comparative analysis. Finally, the reactants' consumption profile, flux and sensitivity analysis were simultaneously performed for explaining the chemistry behind the blending octane behavior of the PRF blends with 1,3-butadiene and toluene.

Keywords: Blending octane behavior; C_4 hydrocarbons; Ignition delay time; Research octane number; Motor octane number; Chemical kinetics

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1. Introduction

Octane number (ON) is an important indicator of the anti-knock quality of commercial gasoline fuels. It is experimentally measured in a Cooperative Fuel Research (CFR) engine under two standard operating procedures: ASTM D2699 [1] and ASTM D2700 [2], resulting in the research octane number (RON) and motor octane number (MON) respectively. Primary reference fuels (PRF) is the simplest surrogate used for representing a real gasoline fuel, which are binary blends of iso-octane and n-heptane. By definition, the RON and MON values assigned for iso-octane and n-heptane are both 100 and 0 respectively. In addition, the difference and average values between the two properties are defined as octane sensitivity (S = RON - MON) and anti-knock index (AKI = (RON + MON) / 2) respectively. In order to match the octane sensitivity of a commercial fuel, toluene primary reference fuel (TPRF) is another commonly used simple gasoline surrogate, which is a ternary mixture of PRF-components and toluene. Toluene is a highly unsaturated hydrocarbon or aromatic hydrocarbon, with the RON and MON values of 120 and 109 respectively [3].

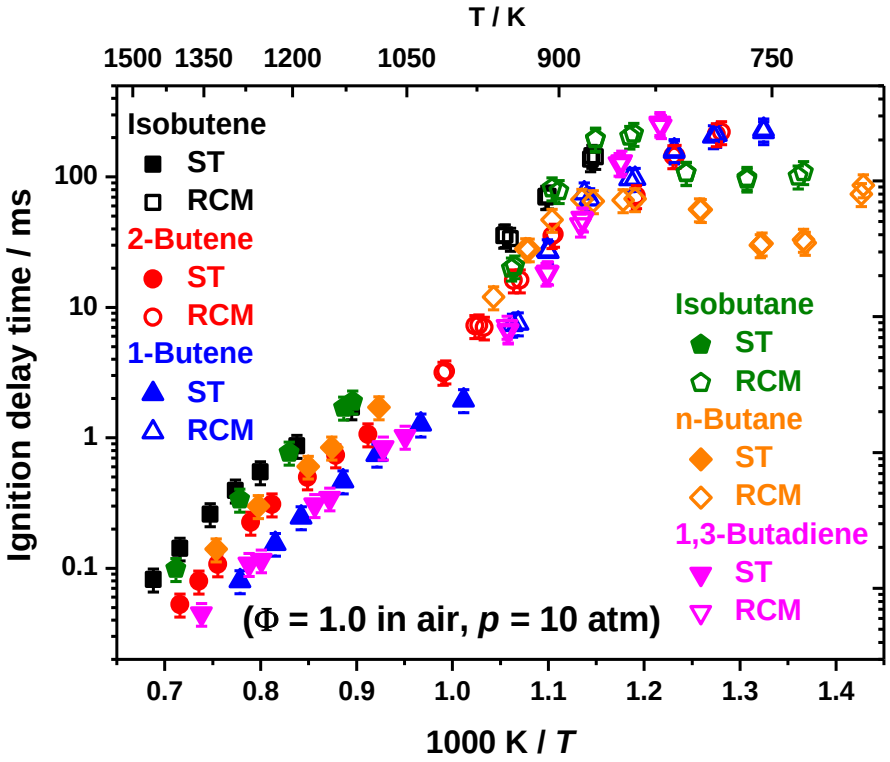
In general, for paraffinic PRF blends, S is equal to 0. While for other types of mixtures (molecules with unsaturated structures or involving heteroatoms), S can be greater than 0, which is mainly attributed to the significantly less pronounced negative temperature coefficient (NTC) behavior i.e. their high resistance to auto-ignition under the test condition of RON than MON [4]. Therefore, the blending octane behavior or knock propensity of a surrogate mixture is closely related to its fundamental gas-phase oxidation chemistry. Recently, Andrae *et al.* [5] and Kang *et al.* [6] have investigated the reactivity effect when adding the unsaturated and branched hydrocarbons (diisobutylene) to PRF surrogate. C_4 hydrocarbons: butane isomers (n-butane and isobutane), butene isomers (1-butene, 2-butene and isobutene) and 1,3-butadiene are the smallest hydrocarbons with both isomeric and conjugated bond structures, which makes them good candidates for understanding the blending octane behavior of unsaturated hydrocarbons by exploring their fundamental chemical kinetics. Therefore, this aim of this study is four-fold:

- Use detailed chemical kinetic models to predict the IDTs of PRF plus C_4 hydrocarbon blends at various temperature and pressure conditions
- Correlate the calculated IDTs with the octane number (RON and MON) at the optimal temperature and pressure conditions
- Formulate the corresponding PRF plus toluene (TPRF) blends by matching the octane number of PRF plus C_4 hydrocarbon blends
- Analyze and identify the important chemical kinetics behind the octane numbers of all PRF plus C_4 hydrocarbon and TPRF blends

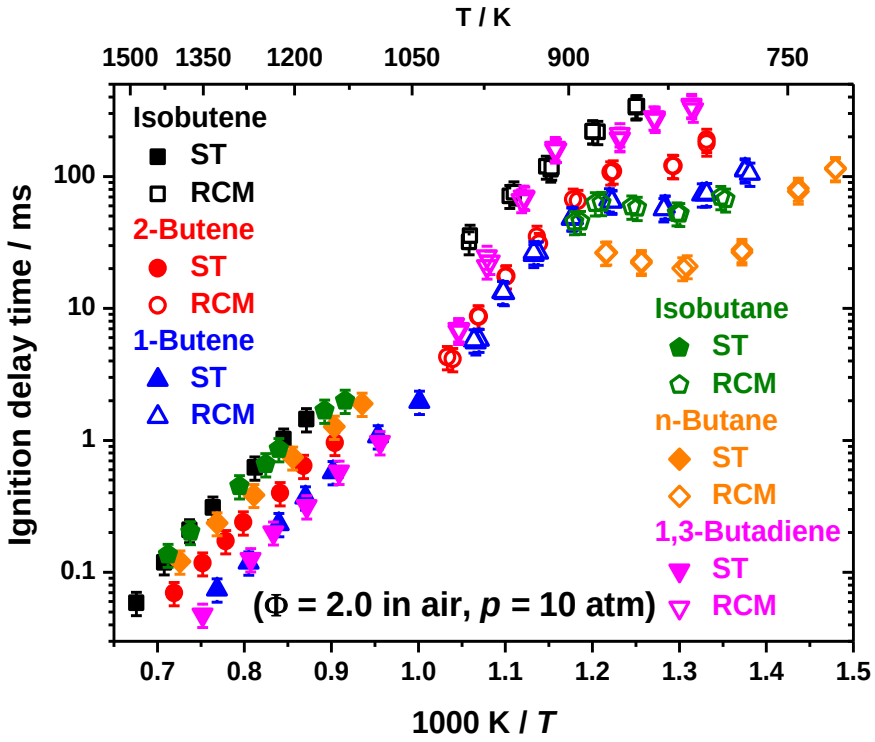
2. Ignition delay time comparisons

Ignition delay time (IDT) is an important indicator for evaluating the global reactivity of a fuel. Some recent IDT measurements in shock tube (ST) and rapid compression machine (RCM) under different conditions (equivalence ratio, pressure and temperature range) and detailed chemical kinetic model studies of C_4 hydrocarbons oxidation are summarized in Table S1 in the Supplementary Material 1. Figure 1 compares the IDTs of the six C_4 hydrocarbons under the two identical conditions: (a) φ = 1.0 and p = 10 atm; (b) φ = 2.0 and p = 10 atm respectively. In the figure, different colors represent the data for different species, and solid and open symbols correspond to the data taken from ST and RCM respectively. It can be seen that the six species exhibit different IDTs because of the difference in molecular structures. At high temperature (1000 – 1400 K), branched- and symmetric-structured molecules (isobutane and isobutene) show longer IDTs than linear- and symmetric-structured molecules (n-butane and 2-butene), with the linear- and asymmetric-structured molecule (1-butene) and linear- and conjugated -structured molecule (1,3-butadiene) being the most reactive. However, quantitatively, the difference between each other is only about a factor of two under the same temperature. At low temperature (700 – 900 K), degrees of branching, symmetry and unsaturation again play an important role on the ignition behavior of six species. The intensity of the negative temperature coefficient (NTC) is roughly in this order: n-butane > isobutane > 1-butene > 2-butene > isobutene ≈ 1,3-butadiene. Molecules with higher degrees of linearity and longer length of

alkylic chain reveal stronger alkyl radical type low-temperature oxidation chemistry, which leads to more pronounced NTC behavior.



(a) φ = 1.0



(b) φ = 2.0

Figure 1. Ignition delay time comparison of C_4 hydrocarbons oxidation at 10 atm. n-Butane, isobutane, isobutene, 2-butene, 1-butene and 1,3-butadiene data are taken from Healy *et al.* [7], Healy *et al.* [8], Zhou *et al.* [9], Li *et al.* [10], Li *et al.* [11] and Zhou *et al.* [12] respectively.

3. Model validation and comparison

In this section, two recently developed detailed kinetic models are selected from literature for estimating the IDTs of six C_4 hydrocarbons, their mixtures with PRF60 and TPRF blends. They are named as AramcoMech 3.0 [12] and KAUST model [13] respectively, as summarized in Table 1. All the models were well validated for IDT's of the containing species among C_4 hydrocarbons (butane isomers, butene isomers and 1,3-butadiene) and TPRF components (iso-octane, n-heptane and toluene) for a wide range of temperatures, pressures and equivalence ratios. In order to predict the IDTs of the mixture of PRF60 plus C_4 hydrocarbons and TPRF blends, a new model was generated by merging the KAUST and AramcoMech 3.0 mode. The model is named as KAUST_AramcoMech model and contains 2317 species and 9699 reactions. The model in CHEMKIN format is provided in the Supplementary Material 2.

Table 1. Three kinetic models selected from literature.

NO.	Reference	Year	Name	Component
1	Zhou *et al.* [12]	2018	AramcoMech 3.0 model	All C_4 hydrocarbons
2	Atef *et al.* [13]	2017	KAUST model	TPRF

It is worth mentioning that the original KAUST model [13] was developed on the basis of AramcoMech 2.0 model [10]. Hence, merging was done by adding the updated 1,3-butadiene sub-mechanism into the KAUST model. In order to confirm the accurate preservation of chemistry in the merged model, the IDT simulation results were compared between the original models (KAUST and AramcoMech 3.0 model) and merged model (KAUST_AramcoMech model) under the typical condition of $\varphi = 1.0$ and $p = 20$ atm, as shown in Figure 2. All IDT simulations, rate of production (ROP), flux and sensitivity analysis were carried out using the ANSYS CHEMKIN- PRO [14] software package. In the figure, different colors and line types denote different species and models, respectively. Excellent repeatability was observed between the two models for all species (toluene,

1,3-butadiene and PRF60) across a wide range of temperatures, which testifies to the validity of the merging process.

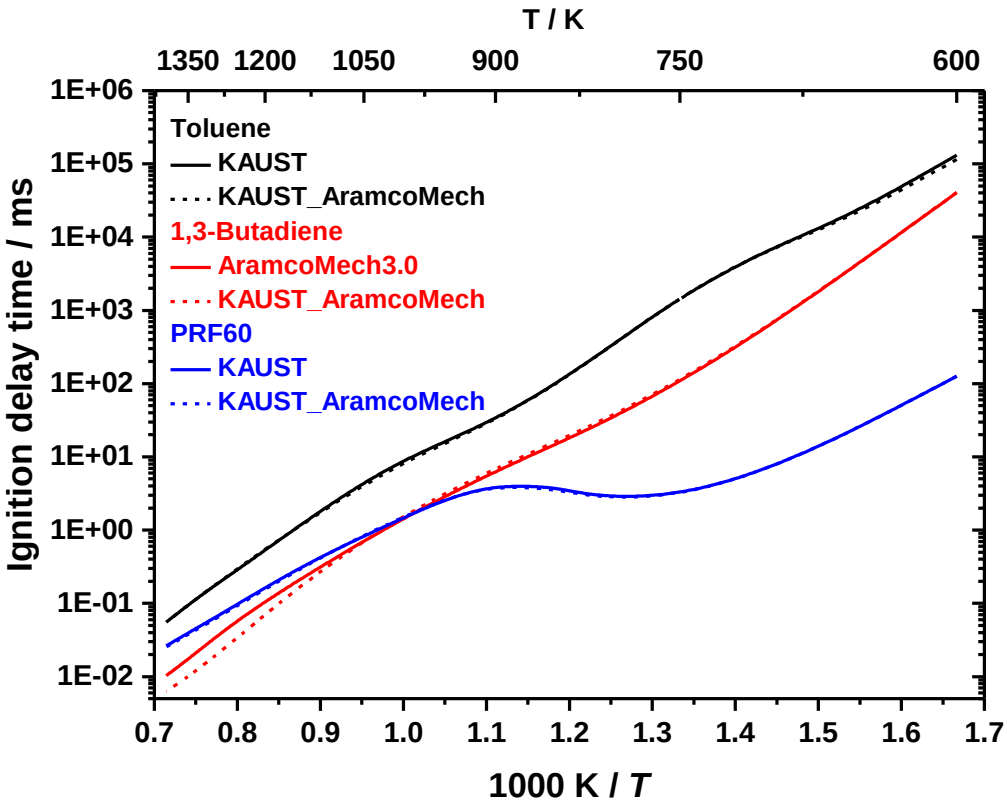
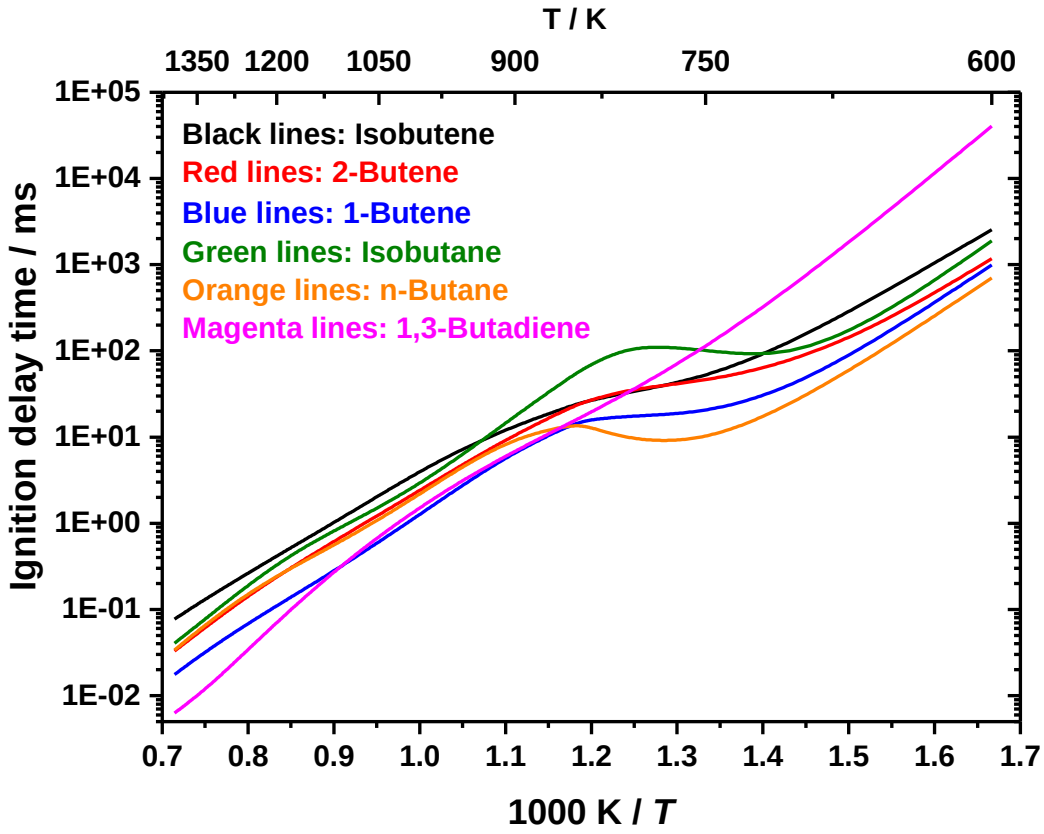


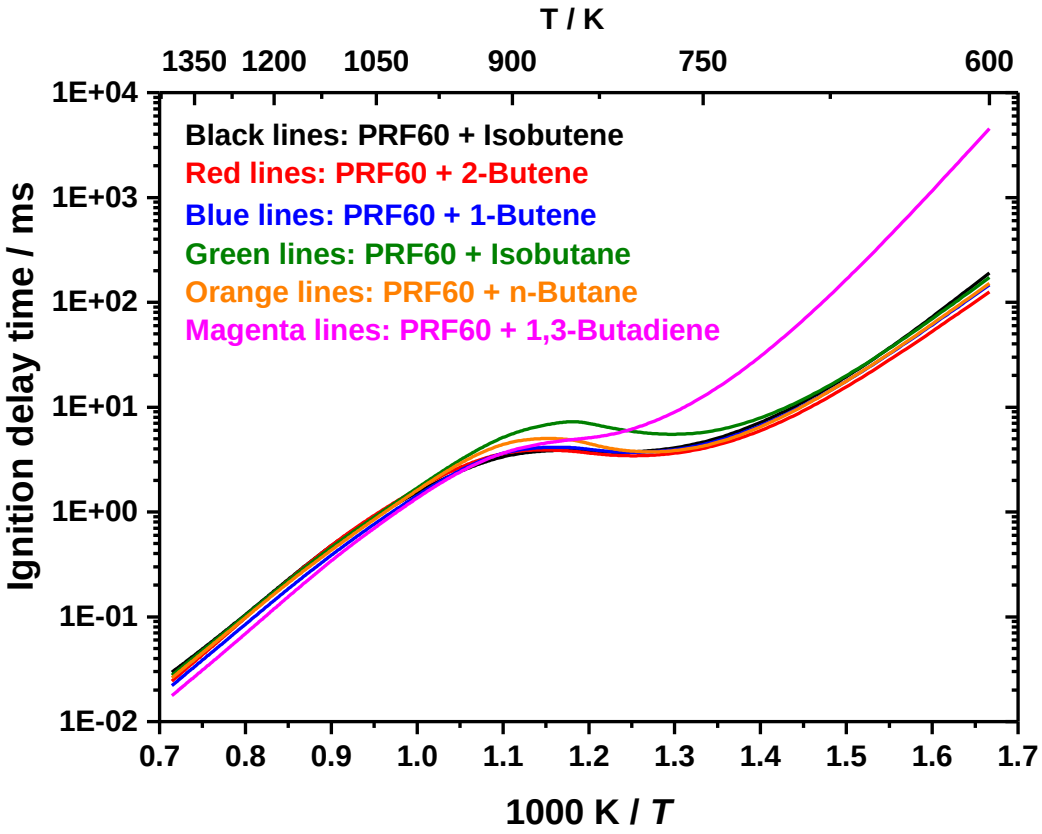
Figure 2. IDT comparisons between original models and merged model.

The merged model was then used to predict the IDTs of pure C_4 hydrocarbons and PRF60 plus C4 hydrocarbons mixtures across wide range of pressures (20 – 50 atm) and temperatures (600 – 1400 K) extensively. All the simulations were performed with a constant volume batch reactor model at equivalence ratio of 1.0 and the pressure and temperature steps were set as 5 atm and 10 K, respectively. All data has been summarized in the Supplementary Material 3. Here, p = 20 atm and T = 600 – 1400 K case is taken as a representative to show the IDT/reactivity comparison of different blends, as shown in Figure 3. In the figure, different colors correspond to different reactants. Among the pure C_4 hydrocarbons, two saturated hydrocarbons: n-butane and isobutane show the most distinct NTC behavior. With the highest degree of unsaturation in the structure, 1,3-butadiene exhibits a linear relationship between its IDT and reciprocal of temperature, which results in a much longer IDT or lower reactivity towards low temperature (< 750K) than all other C_4 hydrocarbons. This is also observed in the comparison of PRF60 plus C_4 hydrocarbons mixtures case, quantitatively, at the lowest

temperature being simulated (600 K) with the IDT difference between 1,3-butadiene and the rest of C_4 hydrocarbons is about a factor of 13.



(a) 100% C_4 hydrocarbons



(b) 80% PRF60 + 20% C_4 hydrocarbons

Figure 3. IDT comparisons for pure C_4 hydrocarbons and PRF60 plus C_4 hydrocarbons mixtures.

4. RON and MON predictions

Table 2 summarizes the octane numbers of all C_4 hydrocarbons and relevant mixtures, which were obtained from the American Society for Testing Materials (ASTM) [15], Puckett *et al.* [16], Clifford *et al.* [17], Boldt *et al.* [18] and Morganti *et al.* [19]. In the table, the RON and MON are shown for a) pure C_4 hydrocarbons; b) 80% PRF60 + 20% C_4 hydrocarbons; c) blending octane number. Here, PRF60 stands for the 60:40 mixture of iso-octane and n-heptane by volume, and the blending octane number (BON) is a hypothetical value obtained by extrapolating from the octane number of 20% concentration (by volume) of C_4 hydrocarbons to the value at 100% concentration. It can be seen that, in general, both RON and MON increase with the increasing degrees of branching and unsaturation, and 1,3-butadiene is found to be the strongest octane booster.

Table 2. Octane number of all C4 hydrocarbons and relevant mixtures (ASTM [15], Puckett *et al.* [16], Clifford *et al.* [17], Boldt *et al.* [18] and Morganti *et al.* [19]).

Species	100% C_4	80% PRF60 + 20% C_4	Blending octane number
RON			
n-Butane	93.5	70.6	113
iso-Butane	100.1	72.4	122
1-Butene	97.4	76.7	144
2-Butene	99.6	78.4	152
iso-Butene	-	81.9	170
1,3-Butadiene	-	87.1	196
MON			
n-Butane	89.0	70.7	114
iso-Butane	96.8	72.1	120
1-Butene	81.7	73.2	126
2-Butene	-	73.6	128
iso-Butene	-	75.8	139
1,3-Butadiene	-	76.8	144

In order to correlate the calculated IDTs in last section with the octane numbers shown in Table 2, three sets of recently developed empirical equations were selected from literature: Badra *et al.* [20], Singh *et al.* [21] and Naser *et al.* [22], and they were summarized in Table S3 in the Supplementary Material 1. It is worth mentioning that all equations summarized in Table S3 were developed based on the IDTs simulated under the identical pressure of 25 atm, however, these simulations were performed using different kinetic models, different reactant mixtures and used different expressions (3-, 2-terms natural logarithm, or exponential functions).

In this study, we employed all three sets of equations using the extensive IDTs obtained under wide range of temperature and pressure conditions as input, both RON and MON of the six PRF60 + C_4 hydrocarbon blends were predicted based on the merged model: KAUST_AramcoMech, all results were summarized in the Supplementary Material 3. Root Mean Squared Error (RMSE) was evaluated

between the octane numbers obtained from literature (shown in Table 2) and predicted using different equations based on the IDTs calculated by the merged kinetic model comprehensively for the PRF60 and six PRF60 + C_4 hydrocarbons blends.

Table 3 shows the best correlation conditions and the corresponding RMSE errors for different equations and different kinetic models, for both RON and MON predictions. Overall, the RMSE errors were found to be within 7.0, which is quite small. In addition, these corrections were found to be more reliable at relatively lower pressures (20 and 25 atm) among the extensive pressures (20 – 50 atm) being investigated. Finally, the best correlation conditions were summarized as: (a) Badra *et al.* at the condition of p = 25 atm and T = 760 K; (b) Singh *et al.* at the condition of p = 20 atm and T = 770 K, therefore, they will be used for analyzing the fundamental chemistry in section 5.

Table 3. Best correlation conditions and the corresponding errors.

Correlation equations	Condition	Error
Badra *et al.*	p = 25 atm and T = 760 K	5.4 and 5.2
Singh *et al.*	p = 20 atm and T = 770 K	5.8 and 4.8
Naser *et al.*	p = 20 atm and T = 740 K	6.9 and 5.4

Among the six C_4 hydrocarbons, 1,3-butadiene with the conjugated bond structure, was found to be the strongest octane enhancer. Based on this, it would be interesting to see how a further increased degree of unsaturation of a hydrocarbon can affect its blending octane behavior with PRF. Toluene is a highly unsaturated hydrocarbon as well as a simple aromatic compound, which is also commonly used as an octane/sensitivity enhancer. Apart from the IDT-based correlation discussed above, Morgan *et al.* [3] and Kalghatgi *et al.* [23] have recently developed a second-order polynomial and linear-by-volume (LbV) correlations to map the composition of TPRF (PRF + toluene) surrogate based on the given RON and MON. Therefore, a TPRF blend was proposed by matching the octane number of the "80% PRF60 + 20% 1,3-Butadiene" mixture shown in Table 2. Table 4 shows the composition (volume ratio) and octane number of the two mixtures. It can be seen that TPRF blend has significantly higher amounts of iso-octane in PRF, and higher amount of toluene versus 1,3-butadiene, this clearly

indicates that 1,3-butadiene with less degree of unsaturation, has higher ability of boosting the octane number than toluene. The detailed chemistry behind this will be discussed in the following section.

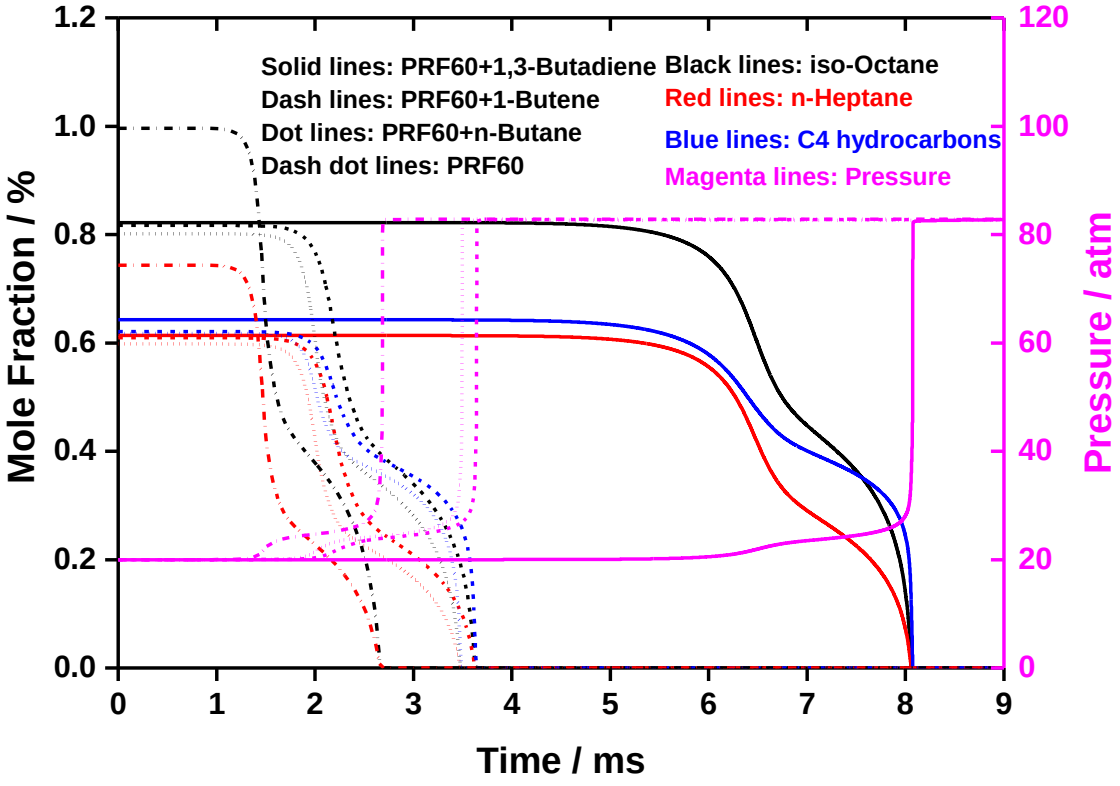
Table 4. The octane number and composition of PRF + 1.3-butadiene and PRF + toluene blends.

	80% PRF60 + 20% 1,3-Butadiene	TPRF
iso-Octane	48%	61.2%
n-Heptane	32%	7.9%
1,3-Butadiene	20%	-
Toluene	-	30.9%
RON	87.1	86.9
MON	76.8	77.0

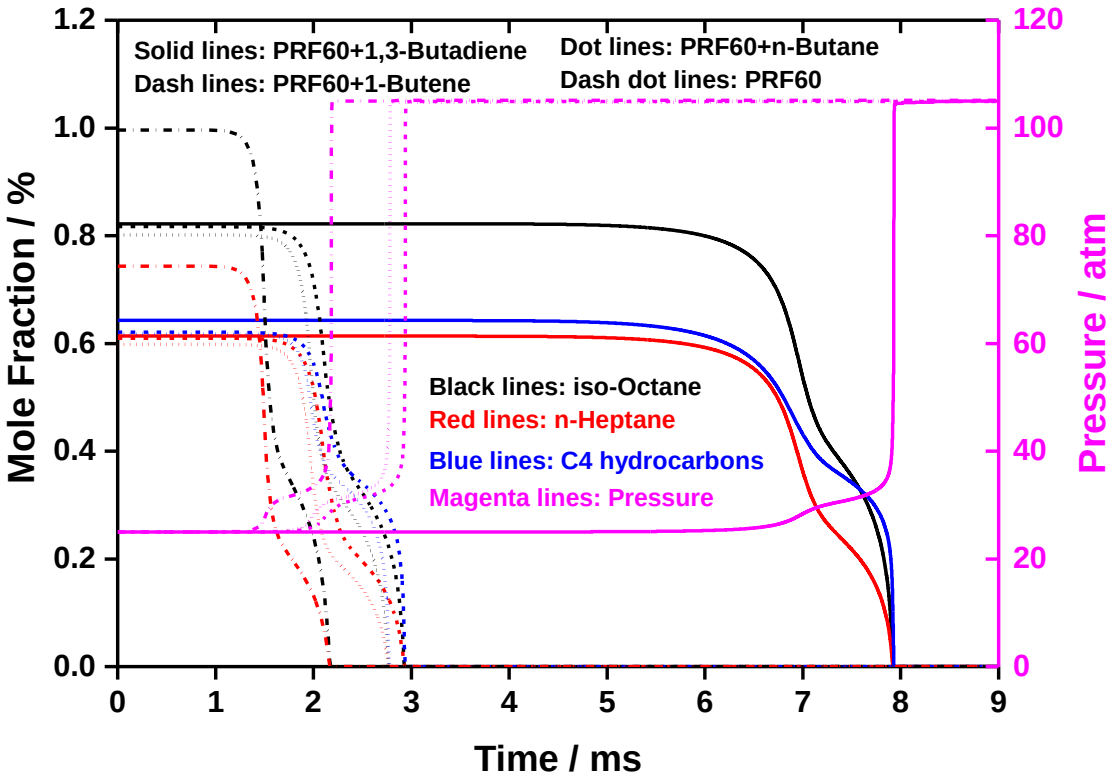
5. Chemical kinetics analyses

In order to investigate the chemistry behind the observed phenomena discussed in the last three sections, the reactants' consumption profile, flux and sensitivity analyses were simultaneously performed to identify the important chemical reactions for all six PRF60 plus C_4 hydrocarbon mixtures as well as the TPRF blend. Firstly, we took the PRF60 and PRF60 + linear C_4 hydrocarbons (1,3-butadiene, 1-butene and n-butane) blends as representatives, the rate of production (ROP) analysis was performed using the merged model under the two best correlation conditions: (a) p = 20 atm and T = 770 K; (b) p = 25 atm and T = 760 K, as shown in Table 3. Figure 4 shows the reactants' consumption profiles predicted for the reactants of the four mixtures. In the figure, different line types and colors stand for different mixtures and the different components in each mixture respectively, and the pressure traces are in magenta color corresponding to the y-axis at right side. All mixtures exhibit two-stage ignition events which can be attributed to the low-temperature oxidation chemistry of saturated alkyl radicals from iso-octane and n-heptane. PRF60 plus 1,3-butadiene blend exhibits the longest consumption time (about 8 ms) among all mixtures. Therefore, flux analysis was performed for this

particular blend at the timing of the rapid decay of reactants after the first stage ignition, which is around 7 ms.



(a) p = 20 atm and T = 770 K



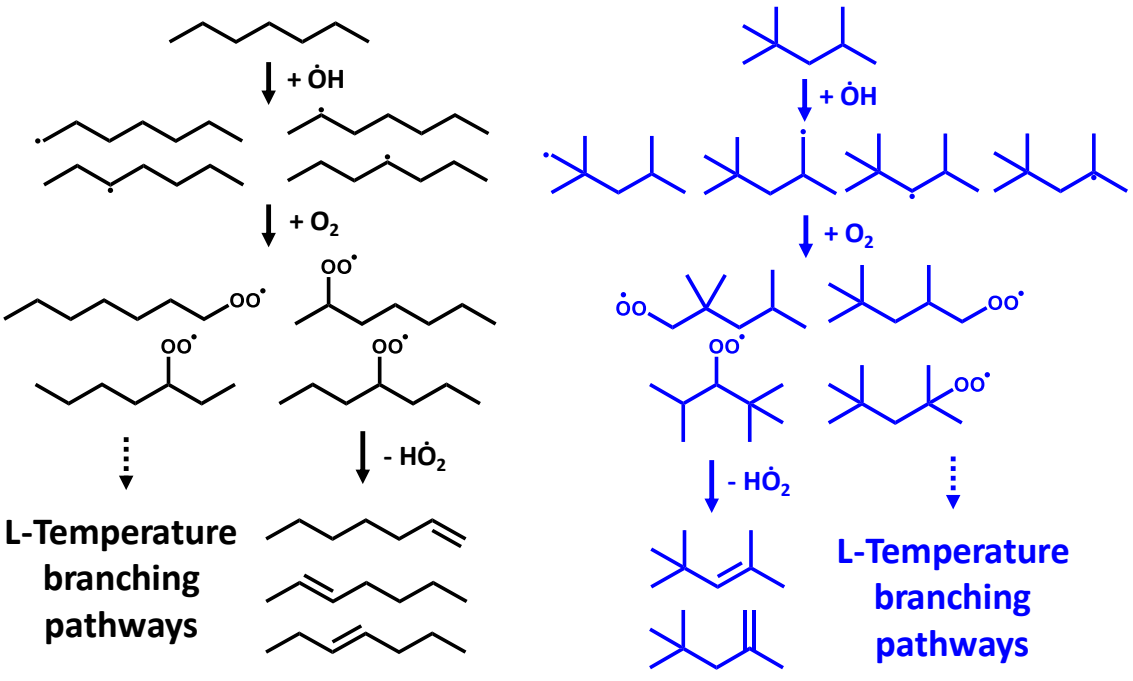
(b) p = 25 atm and T = 760 K

Figure 4. Reactants' consumption profile analysis for PRF60 and PRF60 plus C_4 hydrocarbon mixtures.

Figure 5 shows the flux analysis results for the PRF60 plus 1,3-butadiene blend, notably, in order to make the results more visualized, only the qualitative or generalized reaction pathways were exhibited in the figure, while the quantitative values for the flux of all reactions have been gathered in the Supplementary Material 4. As can be seen, both iso-octane and n-heptane exhibit typical alkyl radical low temperature chemistries, the competition between the HO_2 radical concerted elimination from RO_2 and RO_2 isomerization to QOOH leads to the NTC behavior. However, the oxidation chemistry of 1,3-butadiene is much more complex, fuel initiation chemistry contains two major reaction routes: (a) H-atom abstraction by ȮH radical; (b) ȮH radical addition to the C=C double bond, moreover, both routes can occur at two sides: terminal and central carbon atoms respectively. The abstraction reaction route generates two butadiene radicals (iso and normal), followed by the molecular oxygen or hydroperoxyl radical addition, while H-atom abstraction from the central carbon atom is

favored, since for the bond dissociation energy (BDE) of the C-H bond in 1,3-butadiene, secondary allylic-vinylic site (101.5 kcal mol^{-1}) is significantly lower than primary vinylic site (110.5 kcal mol^{-1}), which was calculated by Li *et al.* [24]. The addition reaction route is dominant at low temperature (T < 900 K), however, ȮH radical adding to the terminal and central carbon atoms produce two different radicals, which further lead to two disparate reaction mechanisms. ȮH radical addition to the terminal carbon atom forms a resonantly-stabilized alcohol radical ($C_4H_6$4,2-1OH), which is a favored path inhibiting the reactivity, while central carbon addition reaction generates an alcoholic alkene radical ($C_2H_3CHOHCH_2$), which will subsequently undergo either $HȮ_2$ radical concerted elimination or typical Waddington mechanism forming small aldehydes, ketones and ȮH radical.

To summarize, the two favored reaction pathways for the 1,3-butadiene oxidation have been circled/highlighted in Figure 5, both pathways inhibit the reactivity and consume vast amount of $HȮ_2$ radical during the radical propagation process. At the same time, the concerted elimination reaction of RO_2 radicals in PRF blend represents a major source $HȮ_2$ radicals, therefore, the equilibrium of this reactivity inhibiting reaction would be shifted to the product side, which results in a second round reactivity inhibiting effects.



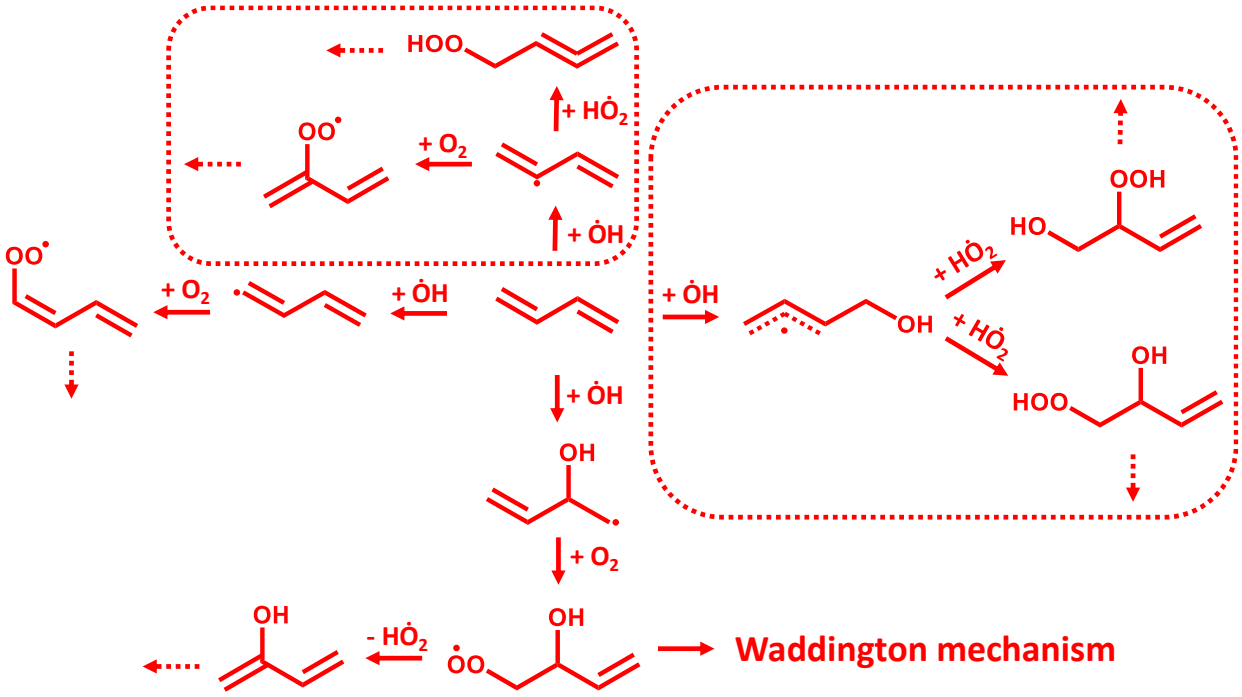
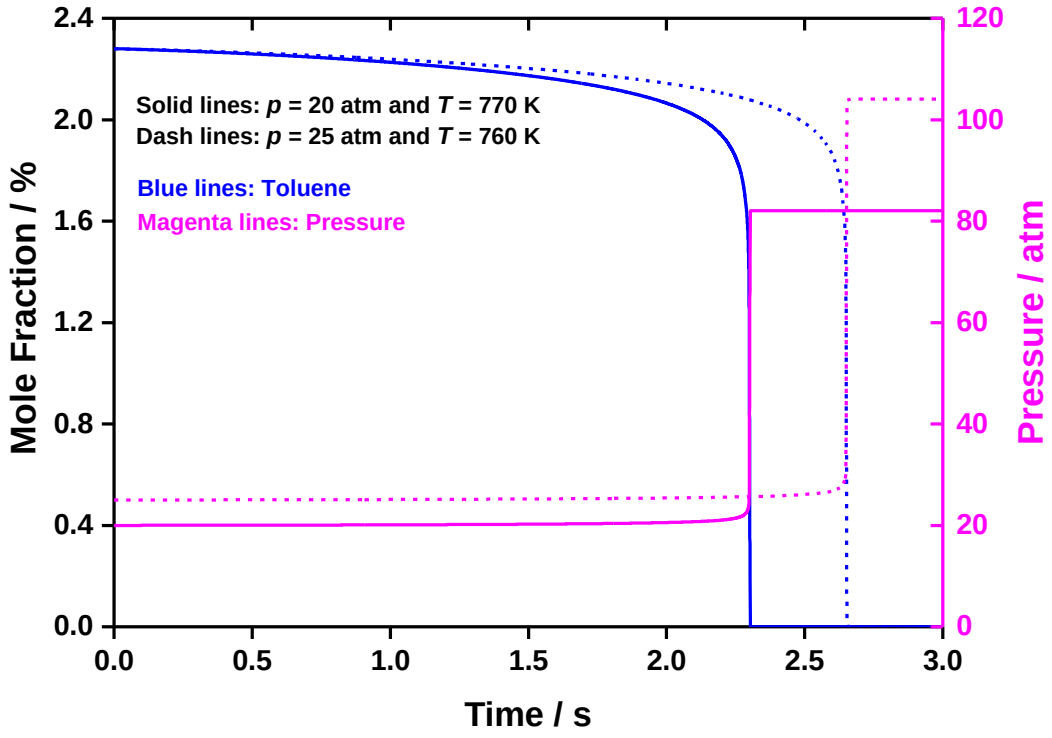


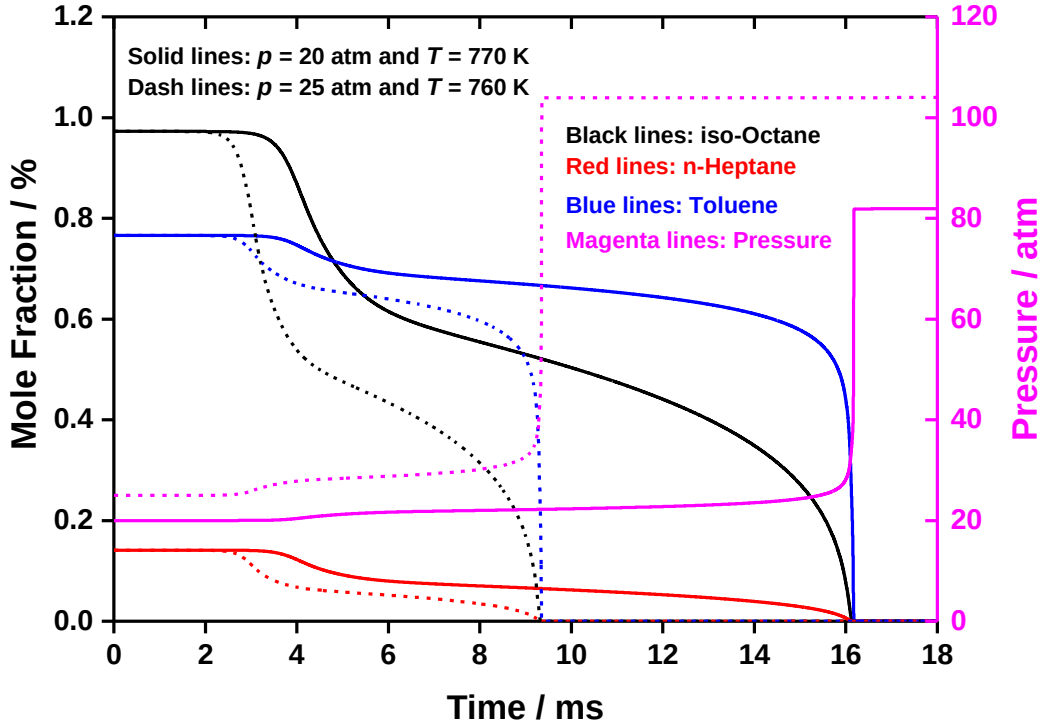
Figure 5. Major paths involved in the ignition of the PRF60 plus 1,3-butadiene blend (p = 25 atm, T = 760 K and t = 7 ms).

Furthermore, the reactants' consumption profile, flux and brute force sensitivity analysis [11] have all been carried out for both pure toluene and the proposed TPRF blend (shown in Table 4) under the two best conditions simultaneously. The reactants' consumption profile and sensitivity analysis were shown in Figure 6 and Figure 7 respectively. From the reactants' consumption profile, it can be seen that, after blending toluene with PRF, the two-stage ignition event was again clearly observed. In addition, the proposed TPRF blend predicts equivalent IDT (about 9 ms) with the "PRF60 plus 1,3-butadiene blend" at 25 atm and 760 K, which testified the reliability of the second-order polynomial correlation discussed in last section. From the sensitivity analysis, it can be seen that, the most inhibiting reaction is the fuel initiation chemistry: H-atom abstraction from the allylic H-atom on the methyl group by ȮH radical forming the benzyl radical ($C_6H_5CH_2$). Thereafter, the reactions between the formed benzyl radical ($C_6H_5CH_2$) and $H\dot{O}_2$ radical on the potential energy surface (PES) of $C_6H_5CH_2OOH$ took over the dominance, the association reaction forming benzyl-peroxy (BZCOOH) and chemical activation reaction forming benzoxy radical ($C_6H_5CH_2\dot{O}$) plus ȮH radical became the top reactivity inhibiting and promoting reactions respectively. Of interest is that sensitivity analysis

results shows that by mixing the PRF with toluene, the main promoting reaction, namely allylic H-atom abstraction by molecular oxygen ($C_6H_5CH_3 + O_2 \leftrightarrow C_6H_5CH_2 + HO_2$) turned into an inhibiting reaction, as highlighted in red rounded rectangles.



(a) Pure toluene



(b) TPRF blend

Figure 6. Reactants' consumption profile analysis for pure toluene and TPRF blend.

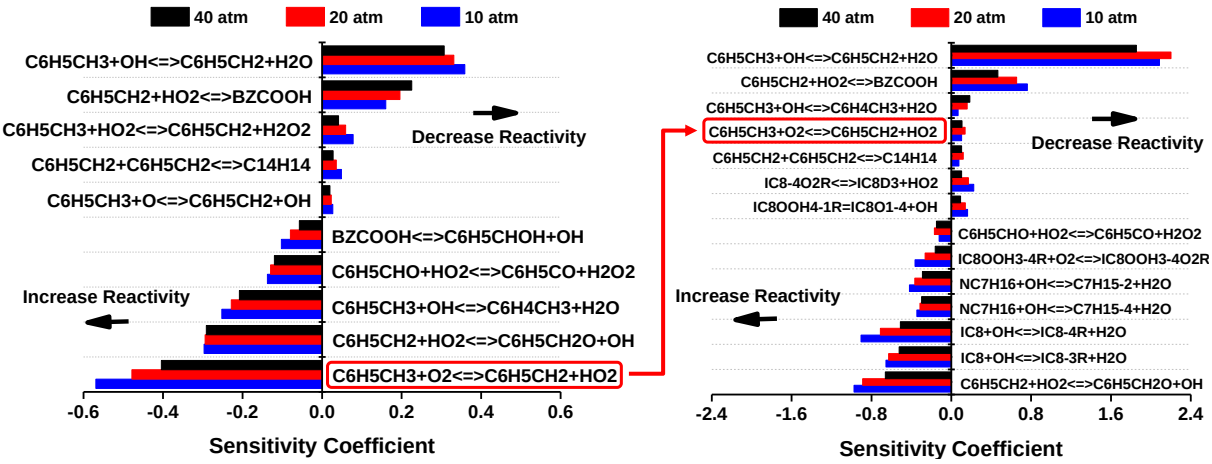


Figure 7. Sensitivity analysis for pure toluene and TPRF blend (T = 760 K).

Figure 8 shows the flux analysis results, which are the generalized reaction pathways for the toluene oxidation chemistry in the TPRF blend. It shows that this abstraction reaction actually occurs in the reverse direction. To summarize, by blending toluene with PRF, $H\dot{O}_2$ radical can be sourced from the concerted elimination reaction of RO_2 radicals from the iso-octane and n-heptane oxidation. Then it reacts with benzyl radical ($C_6H_5CH_2$) via association or chemical activation reactions on the $C_6H_5CH_2OOH$ PES, or reacts reversely to give initial reactants (toluene and molecular oxygen), which is different from the 1,3-butadiene oxidation chemistry.

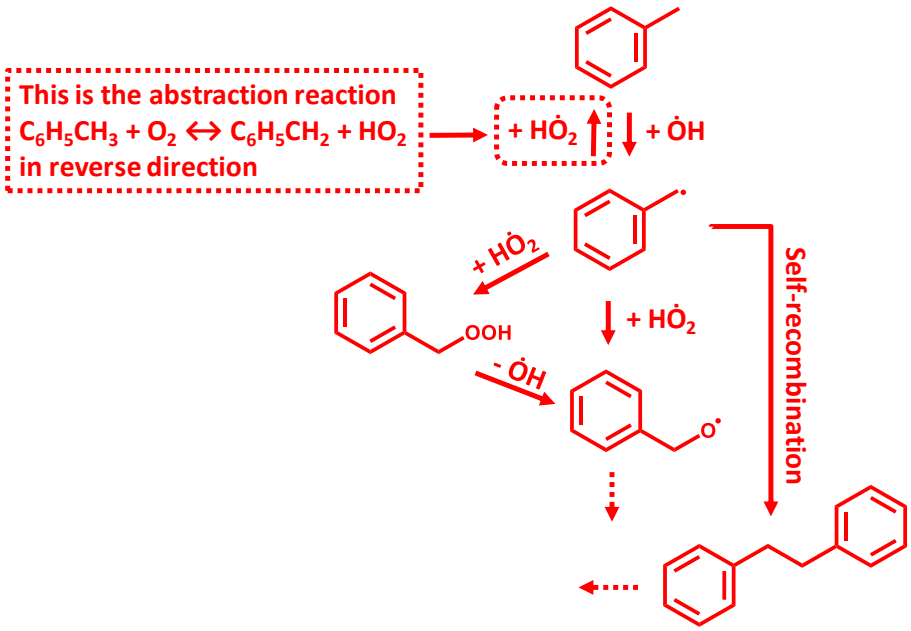


Figure 8. Flux analysis for the toluene oxidation chemistry in the TPRF blend (p = 25 atm, T = 760 K and t = 4 ms).

6. Conclusions

This study provided a systematic investigation of the blending octane behavior of C_4 hydrocarbons (n-butane, isobutane, 1-butene, 2-butene, isobutene and 1,3-butadiene), as well as their comparison with toluene. Investigations were carried by comparing experimentally measured RON and MON obtained from literature with detailed chemical kinetic simulations. Empirical correlation equations were employed to link fundamental chemistry with practical gasoline engine related octane numbers. Below are some of the important findings:

- The two best correlations between the octane number and homogeneous IDTs are: (a) the equations from Badra *et al.* at the condition of p = 25 atm and T = 760 K; (b) the equations from Singh *et al.* at the condition of p = 20 atm and T = 770 K. The standard errors for both are within 6.0.
- With the highest degree of unsaturation in its structure, 1,3-butadiene was found to be the strongest octane enhancer among all C_4 hydrocarbons, and it is also stronger than toluene.
- On analyzing the oxidation chemistry behind above phenomenon, $H\dot{O}_2$ radical reacting with allylic radical (C_4H_5-I, $C_4H_6$4,2-1OH and $C_6H_5CH_2$) plays a key role on the blending octane behavior of unsaturated hydrocarbons. In 1,3-butadiene oxidation, the major reactivity inhibiting reaction pathways are: $\dot{O}H$ radical addition to the terminal carbon atom and H-atom abstraction from the central carbon atom. At the same time, the aforementioned reaction pathways further inhibit oxidation pathways in PRF components, iso-octane and n-heptane, namely: concerted elimination reaction of RO_2 radical forming the $H\dot{O}_2$ radical. In toluene oxidation, $H\dot{O}_2$ radical was only involved in the reaction with the benzyl radical ($C_6H_5CH_2$); however, three different reaction types were found to control its reactivity: (a) association reaction forming the benzyl-peroxy (BZCOOH); (b) chemical activation reaction forming the benzoxy radical ($C_6H_5CH_2\dot{O}$) plus $\dot{O}H$; (c) reverse reaction of H-atom abstraction from methyl group by molecular oxygen ($C_6H_5CH_3 + O_2 \leftrightarrow C_6H_5CH_2 + HO_2$).

From the application point of view, the merged kinetic model together with the correlations provide a way of predicting the octane number when blending 1,3-butadiene with simple gasoline surrogates, as well as understanding the interaction between olefins and alkanes in a commercial gasoline. At the same time, understanding of the fundamental oxidation chemistry of highly unsaturated hydrocarbons can be used for developing other relevant potential octane boosters in future.

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Supplementary Material 1: Additional information

Supplementary Material 2: Merged kinetic model

Supplementary Material 3: Calculated IDTs and ROM/MON correlations

Supplementary Material 4: Reactants' consumption profile and flux analysis results

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