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On the super adiabatic flame temperature (SAFT) of toluene primary reference fuels

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ABSTRACT

Toluene primary reference fuel (TPRF) mixtures containing iso-octane (i- C_8H_{18}), *n*-heptane (n- C_7H_{16}), and toluene (C₆H₅CH₃) are commonly used as gasoline surrogates. We report the occurrence of super adiabatic flame temperature (SAFT) during the premixed combustion of TPRF mixtures in air. Both 1-D premixed flame and 0-D (well-stirred) reactor configurations have been considered for chemical kinetic analysis with Cantera version 2.5.1. A recently developed detailed gasoline surrogate mechanism (C3MechV3.3) has been used for the 0-D reactor analysis. On the other hand, the flame structures have been simulated with a skeletal mechanism. To ensure accurate analysis, the mechanisms used in this work have been validated at SAFT relevant conditions against experimental data from literature. For the first time in literature, post-flame heat release and brute force reaction sensitivity analysis have been performed to identify important reactions contributing towards SAFT in TPRF surrogates. The degree of superadiabaticity for 1-D and 0-D cases have been expressed with nondimensional parameters ξ_{1D} and ξ_{0D} respectively. The results show that ξ_{1D} and ξ_{0D} increase with the increase in iso-octane content in TPRF compositions, while n-heptane and toluene have minor influence on SAFT. Key chemical observations to the SAFT mechanism in gasoline surrogate mixtures include: 1) The competition between the exothermic reaction zone and the endothermic post-flame region causes SAFT. 2) Both 1-D flame and 0-D reactor analysis show that the reactions involving H, OH, and C3 species have major influence on SAFT. 3) Iso-octane augments SAFT as its β -scission product iso-butene (i-C₄H₈) influences the post-flame endothermicity and C3 species formation.

1. Introduction

Light duty vehicles (LDVs) run on gasoline constitute the largest share (around 44 %) of the global transport energy demand [1]. Even with the increase in electric vehicles, it is forecasted that around 32 % of world's transport energy demand will depend on gasoline by 2050 [2]. To achieve higher efficiency from gasoline engines, detailed knowledge of gasoline combustion process is required. Increasingly stringent emission regulations motivate detailed studies on the fuel combustion chemistry. Additionally, modern city traffic conditions often force the engines to operate at transient conditions like cold starting and accelerating. It is very difficult to ensure efficient combustion and lower emission under such conditions. One common feature between the cold starting and accelerating is the use of rich fuel–air mixture, where the fuel quantity exceeds the stoichiometric limit [3]. Moreover, modern gasoline direct injection (GDI) engines utilize stratified charge distribution with a rich core and lean near wall fuel–air mixture inside the cylinder [4].

According to recent literature, the investigations on the combustion of rich hydrocarbon-air mixtures show higher uncertainties in the measured laminar burning velocity values than those at lean and stoichiometric conditions [5]. Chen [6] has shown that the accuracy of the constant volume combustion chamber method for the determination of laminar burning velocity deteriorates significantly in the rich flames for equivalence ratios (φ) beyond 1.2. According to another study by Faghih et al. [7], negative flow speed of the burnt gas reduces flame propagation speed in the constant volume chamber, thus affecting the accuracy of the laminar burning velocity measurement for rich fuel–air mixtures. This negative flow speed is caused by the local flame temperature overshoot from the adiabatic flame temperature limit at rich

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Fig. 1. Process flow chart of the analysis of SAFT during premixed TPRF-air combustion in the present work.

stoichiometric conditions [7]. This temperature overshoot phenomenon causes super adiabatic flame temperature (SAFT) in rich hydrocarbon flames [8,9]. Apart from affecting the accuracy of the constant volume chamber apparatus, SAFT may expand the rich flammability limit of hydrocarbon fuels as well [10,11].

Initially, SAFT was found in the rich premixed flames of acetylene (C_2H_2) -oxidizer mixtures required in the chemical vapor deposition (CVD) process [9,12,13]. Among these works, Bertagnolli and Lucht [12] provided experimental proof of the existence of SAFT with Coherent anti-Stokes Raman scattering (CARS) spectroscopy of hydrogen in a premixed stagnation flame involving acetylene–oxygen–hydrogen mixture. The chemical kinetic analysis performed in these initial works [9,12,13] concluded that (a) SAFT is caused by the delayed decomposition of C_2H_2 that creates a super equilibrium condition in the flame [9] and (b) the super equilibrium condition is also highly influenced by the water (H₂O) and carbon dioxide (CO₂) molecules as their mole fractions exceed the corresponding chemical equilibrium mole fractions [12]. Apart from the analysis of SAFT in CVD

processes, Takagi and Xu [14] observed SAFT in diffusion flames involving methane (CH₄)/hydrogen (H₂)/nitrogen (N₂) mixtures. It was hypothesized in this work [14] that the preferential diffusion of heat and H₂ is responsible for the super equilibrium condition in the flames.

On a similar note, Zamashchikov et al. [15] proposed that the preferential diffusion of H₂ causes SAFT in the rich premixed CH₄ and propane (C₃H₈)-air mixtures. However, this theory was later refuted by Liu and Gülder [8]. According to them [8], the preferential diffusion of H radicals causes its relative scarcity in the premixed flame zone, which in turn results in the overshoot of H₂O, ketene (CH₂CO), and flame temperature. The influence of H radicals on SAFT was later corroborated by Bunev and Babkin [16]. Apart from Liu and Gülder [8], Liu et al. [17,18] have numerically analyzed SAFT for premixed flames involving mixtures of CH₄-air, CH₄-O₂, C₂H₂-H₂-O₂, ethylene (C₂H₄)–O₂, C₃H₈-O₂, and H₂-O₂. It has been concluded from these studies that (a) SAFT does not occur for H₂-O₂ flames [17] and (b) preheat of the unburnt gas suppresses SAFT while an increase in pressure enhances it [18] for rich premixed flames, and (c) the increase of equivalence ratio has a strong positive influence on SAFT in the rich stoichiometric region. Additionally, SAFT has also been reported numerically during the homogenous ignition of CH₄-oxidizer mixtures by Wang et al. [19].

Recently, Sentko et al. [20,21] have experimentally determined SAFT in rich methane-oxidizer flames using gas chromatograph/mass spectrometer (GC/MS) and tunable diode laser absorption spectroscopy (TDLAS). In these works [20,21], the temperature and H₂O concentration (% by volume) were used as the markers for detecting SAFT. It has been shown in one of these works [21] that the equivalence ratio has a stronger influence on SAFT than pressure. Apart from the rich hydrocarbon flames, SAFT has also been reported in ammonia (NH₃)-air [22] and hydrogen azide (HN₃)/N₂ flames [10].

In comparison to light hydrocarbons, the research on the super equilibrium phenomenon of heavier hydrocarbons relevant to commercial gasoline is sparse. The analysis of gasoline flames is complicated because commercial gasoline consists of hundreds of hydrocarbons, among which paraffins, i-paraffins, naphthenes, olefins, aromatics, and oxygenates are the major classes [23]. To alleviate complexities, mixtures of limited number of pure components called surrogates are often used to emulate practical characteristics like laminar burning velocities, autoignition behaviors, octane numbers, and distillation curves [24]. Depending on the desired gasoline properties, the composition of gasoline surrogate is determined as, single-component (i.e., iso-octane [25]), binary mixture (i.e., primary reference fuel [26]), ternary mixture (i.e., toluene primary reference fuel [27]), and multicomponent [28]. While the primary reference fuel (PRF) contains isooctane and n-heptane, the three main classes of real gasoline, i.e., aromatic, *n*-paraffin, and iso-paraffin [29] are represented by toluene (C₆H₅CH₃), *n*-heptane (n-C₇H₁₆), and iso-octane (i-C₈H₁₈) in a toluene primary reference fuel (TPRF) surrogate. These TPRF surrogates can successfully capture the autoignition and laminar burning characteristics of a wide variety of gasoline fuels [24].

There is considerable amount of work on the 1-D flame structure analysis of gasoline and its surrogate components in literature. Some of the early efforts in this regard include the works of Douté et al. [30] and Bakali et al. [31] for flames involving i-C₈H₁₈ and n-C₇H₁₆. In a later study, a rich premixed gasoline-oxidizer flame ($\phi = 1.73$) at low pressure (30 Torr) has been analyzed by Li et al. [32]. In another work, Li et al. [33] measured combustion intermediates up to C₁₉H₁₂ in a lowpressure rich premixed ($\varphi = 1.9$) toluene-oxidizer flame. Zeng et al. [34] have experimentally studied premixed low-pressure flames of i- C_8H_{18} at $\varphi = 1.47$. Similarly in another study by the same group [35], 1-D flame involving n-C₇H₁₆-oxidizer mixture was studied at $\varphi = 1.48$. Osipova et al. [36] have analyzed the rich flame structure of n-C₇H₁₆/ C₆H₅CH₃-oxidizer mixture with a skeletal mechanism from Dirrenberger et al. [37]. Similarly, Dmitriev et al. [38] have analyzed n-C7H16/ C₆H₅CH₃-oxidizer flame with an updated version of the Dirrenberger et al. [37] mechanism. Recently, Zhang et al. [39] have used a stagnated 1-D flame to study the poly-aromatic hydrocarbon (PAH) formation pathways in n-C7H16 flame blended with C6H5CH3 and anisole (C₆H₅OCH₃). However, none of these works have analyzed SAFT for gasoline surrogates. Only recently Han et al. [40] have reported SAFT in flames of gasoline relevant species like i-C₈H₁₈ and n-C₇H₁₆. However, Han et al. [40] only mentioned SAFT as an identification for over-rich region of iso-octane and n-heptane-air flames without any further indepth analysis of its behavior.

It is clear from the above literature review that the SAFT phenomenon has mostly been studied for premixed flames of smaller hydrocarbons, ammonia, and hydrogen azide. As SAFT has been observed to be enhanced by increased equivalence ratio and pressure for lighter hydrocarbon fuels, the combined effect of boosting, charge stratification, cold start, and acceleration has the potential to increase SAFT in modern gasoline engines also. It may be noted here that gasolines primarily consist of high molecular weight hydrocarbons [24]. Despite many studies on 1-D rich premixed flames of gasoline and its surrogate species, the SAFT for gasoline surrogates is still unexplored. Furthermore, the experimental determination of SAFT requires extremely difficult and precise measurement of the temperature profile in 1-D flames [12,20,21]. Even for such experiments, the interpretation of the results must be done through a comprehensive chemical kinetic analysis.

In the present work, we aim to reveal the chemistry behind the SAFT of premixed flames involving TPRF surrogates for gasoline. The investigation has been performed through,

- 1. 0-D chemical kinetic analysis with a detailed mechanism
- 2. 1-D flame analysis with a skeletal mechanism

Finally, the observations from 0-D and 1-D analysis have been combined to provide comprehensive insights into the SAFT of premixed TPRF-air flames.

2. Numerical methodology

Fig. 1 demonstrates the workflow undertaken in this work. Both 0-D and 1-D simulations have been carried out using Cantera 2.5.1 [41] through Python interface. Premixed, freely-propagating, unstretched, and adiabatic conditions are used in Cantera 2.5.1 [41] for the 1-D flame simulations.

The grid convergence has been ensured for an initial domain length of 10 cm with adaptive grid points determined automatically by the solver. The chosen adaptive grid parameters are ratio = 3, slope = 0.1, curve = 0.1, and prune = 0.03 [28]. These parameters ensured final solutions with around 200 grid points. Moreover, the mixture-averaged transport formulation was also included in the computations. With these parameters, the inlet conditions (i.e., unburnt gas temperature, pressure, and equivalence ratio) were varied based on the purpose of simulation. For 0-D simulations, an adiabatic well-stirred reactor (WSR) with constant pressure has been used. In the WSR, the gas mixing is infinitesimally fast with mass flow rate of reactants coming in being constant and equal to that of products going out. The time the gas mixture stays in the reactor is called residence time [42].

The degree of SAFT in 1-D (ξ_{1D}) and 0-D (ξ_{0D}) flames has been calculated with the non-dimensional parameters,

$$\xi_{1D} = \frac{T_{flame,peak} - T_{un}}{T_{eq} - T_{un}} \tag{1}$$

$$\xi_{0D} = \frac{T_{WSR,peak} - T_{un}}{T_{eq} - T_{un}}$$
(2)

Here, $T_{flame,peak}$ is the maximum temperature of the 1-D flame, T_{WSR} , $_{peak}$ is the maximum outlet temperature at a certain residence time from the WSR, T_{un} is the unburnt gas temperature, and T_{eq} is the adiabatic flame temperature achieved with the combustion product gases in chemical equilibrium. For 1-D flames, T_{eq} is assumed to be equal to the temperature at the end point of the computational domain [40]. On the other hand, following the approach of Han et al. [22], T_{eq} has been obtained by minimizing isobaric Gibbs free energy in Cantera [41] for 0-D calculations. The ' ξ ' is shown as a function of ΔT (= $T_{peak} - T_{eq}$) in Fig. 1.

As shown in Fig. 1, the reactions responsible for SAFT have been identified with brute force sensitivity analysis for both 1-D and 0-D analysis. For the 1-D flame, the sensitivity analysis has been performed at the point of maximum temperature in the flame. While the sensitivity analysis has been performed at the residence time corresponding to maximum temperature for the 0-D cases. The sensitivity value is defined as,

$$\Delta_{1D \ or \ 0D} = \frac{\ln(\frac{T_2}{T_{0,5}})}{\ln(\frac{k_2}{k_{0,5}})}$$
(3)

Here, k_2 and $k_{0.5}$ are the rate constants while T_2 and $T_{0.5}$ are the values of maximum temperature with doubled and half specific forward



Fig. 2. Fuel components and C_2H_2 mole fraction profiles obtained using C3MechV3.3 [43] (black solid line), LLNL [44] (red dashed line), and Fang et al. [45] (blue dot line) mechanisms compared with experimental data from Shao et al. [46] for TPRF70 (circle) and TPRF97.5 (triangle) pyrolysis in a jet-stirred reactor (JSR). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

reaction rate, respectively. According to this definition, a positive sensitivity value denotes that the increasing forward reaction rate leads to higher maximum temperature and vice versa. It may be noted that the brute force sensitivity analysis with the detailed mechanism for the 0-D WSR case has been performed in parallel where the reactions were divided into 32 processors. This way, the sensitivity analysis was completed within 10–16 wall clock hours.

3. Selection of mechanisms

As seen from Fig. 1, the initial step towards the chemical kinetic analysis has been to select the best performing mechanism from literature in predicting experimental data at rich stoichiometric conditions relevant to SAFT. First, detailed mechanisms have been compared for WSR simulations. Although these large mechanisms provide chemically accurate simulations, skeletally reduced mechanisms are often used for computational fluid dynamics simulations to keep the computational load within manageable limit. Therefore, skeletal mechanisms have also been compared in the context of rich 1-D premixed flames later in this section.

3.1. 0-D well stirred reactors

Recently developed detailed kinetic models for gasoline surrogates include the mechanisms proposed by Computational Chemistry Consortium (C3MechV3.3) [43] with 3761 species and 16,532 reactions, Lawrence Livermore National Laboratory (LLNL) [44] with 1389 species and 9604 reactions, and Fang et al. [45] with 1543 species and 8743 reactions. In this section, the accuracy of these detailed mechanisms in predicting experimentally obtained species profiles from WSR has been assessed. Shao et al. [46] measured the species profiles during the pyrolysis of two TPRF mixtures (TPRF70 and TPRF97.5) in a jet-stirred reactor (JSR) at P = 1 atm and in the temperature range 800 – 1250 K. The molar composition of i-C₈H₁₈/ n-C₇H₁₆/ C₆H₅CH₃ mixture is 36.5 %/ 35 %/ 28.5 % for TPRF70 and 8 %/ 14.5 %/ 77.5 % for TPRF97.5 respectively. Fuel concentration of 0.25 % and residence time of 1 s were used in conducting the experiments. Comparisons between the experimental measurements [46] and kinetic simulations from literature models are presented in Fig. 2 (a-d).

It can be seen from Fig. 2 (a) that the mole fraction profiles of $i-C_8H_{18}$ for both TPRFs is generally well predicted by the models. At temperature lower than 1010 K, the Fang et al. [45] mechanism predicts $i-C_8H_{18}$ mole fraction more accurately with deviations less than 15 % and 20 % for pyrolysis of TPRF70 and TPRF97.5, respectively, while C3MechV3.3 performs better at higher temperature range. In Fig. 2 (b), mole fraction profiles of n-C₇H₁₆ are also acceptably reproduced by C3MechV3.3 [43] and Fang et al. [45] mechanisms throughout the studied range of temperature for TPRF70 and TPRF97.5 pyrolysis. All three mechanisms perform well in predicting $C_6H_5CH_3$ concentrations at low temperature (*T* less than 1010 K) for both TPRFs in Fig. 2 (c). However, at higher temperatures for TPRF97.5, some deviations are observed for all three mechanisms. For TPRF70, C3MechV3.3 [43] and Fang et al. [45] mechanisms perform better than the LLNL mechanism [44] in predicting the $C_6H_5CH_3$ mole fraction in Fig. 2 (c).

Along with the fuel species, Shao et al. [46] have presented mole fraction profiles of PAHs and lighter gaseous soot precursors like acetylene, allene, prope(y)ne and many more. Therefore, the performance of the mechanisms in predicting the mole fraction profiles of C_2H_2 is shown in Fig. 2 (d). It can be seen from the figure that C3MechV3.3 [43] predicts the mole fraction profiles of C_2H_2 very well in both low and high temperature ranges for TPRF97.5 and TPRF70. On the other hand, the



Fig. 3. Mole fraction profiles of O_2 , H_2O , CO_2 , CO, and C_2H_2 obtained using C3MechV3.3 (black solid line) [43], LLNL (red dashed line) [44] and Fang et al. (blue dot line) [45] mechanisms compared with experimental data from Chen et al. [47,48] (circle for TPRF A and triangle for TPRF F) oxidation in jet-stirred reactor (JSR) at 10 bar pressure and $\varphi = 2.0$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

LLNL mechanism [44] overpredicts and Fang et al. mechanism [45] underpredicts C_2H_2 mole fraction at high temperature range in both TPRF70 and TPRF97.5 pyrolysis. Among the studied mechanisms in Fig. 2, it may be concluded that the C3MechV3.3 [43], being the most

detailed model, predicts the species profiles during the pyrolysis of TPRF70 and TPRF97.5 with the best accuracy.

Next, experimental data and simulation results derived by the three kinetic models [43–45] on detailed speciation profiles of FACE (Fuel for



Fig. 4. Laminar burning velocity obtained using Andrae150 (black solid line) [52], Creck156 (red dashed line) [53] and LLNL312 (blue dot line) [51] mechanisms compared with experimental data from (a) Dirrenberger et al. [37] (circle) and (b) Liao et al. [54] (triangle). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Advanced Combustion Engine) gasoline oxidation have been evaluated in Fig. 3 (a-j). Oxidation experiments have been performed in JSR for alkane-rich FACE gasolines (FACE A and C) at a fuel concentration of 1000 ppm and pressure of 10 bar, constant residence time of 0.7 s, temperature range 530–1250 K, and equivalence ratios (φ) of 0.5, 1.0, and 2.0 by Chen et al. [47]. In another work, Chen et al. [48] presented experimental study on the oxidation of high-octane-number FACE F gasoline at same conditions of [47]. Since the focus of the present work is on fuel-rich combustion of TPRF mixtures, experimental data on mole fraction profiles of FACE A and F at $\varphi = 2.0$ have been selected for the comparison in Fig. 3. The compositions for TPRF surrogates of FACE A and F gasolines have been taken from Badra et al. [49].

As seen from Fig. 3 (a), C3MechV3.3 [43] and Fang et al. [45] model predict the mole fraction profile of O2 for TPRF A oxidation within 20 % range of the experimental data for temperatures below 1130 K. For TPRF F oxidation, most of the predictions by the C3MechV3.3 [43] and Fang et al. [45] model are within 25 % range of the experimental data in Fig. 3 (b). It may be mentioned here that the uncertainty is around 15 % for the apparatus [50]. The products of combustion are shown in Fig. 3 (c-h). Furthermore, Fig. 3 (i-j) compares the performance of the mechanisms [43–45] in predicting the mole fraction profiles of C₂H₂. It can be seen from these figures that throughout the whole studied range of temperature, C3MechV3.3 [43] performs best in predicting the mole fraction profiles. On the other hand, the LLNL mechanism shows the largest deviation between simulation data and experimental measurements for all species considered. It is worth mentioning here that Mehl et al. [51] have also reported deteriorated performance of the detailed LLNL mechanism [44] in the rich side of stoichiometry. Due to the superior performance in predicting species profiles from 0-D pyrolysis and oxidation in WSR, the C3MechV3.3 [43] model has been chosen for further 0-D analysis of SAFT in Section 4.2.

3.2. 1-D premixed flames

Despite the fact that the detailed mechanisms provide chemically accurate predictions, their applications are restricted to only 0-D simulations due to limited computational resources. The skeletally reduced mechanisms are used for solving realistic problems in computational fluid dynamics (CFD). Therefore, the SAFT of gasoline surrogates has been analyzed with skeletal mechanisms in this work also. Such analysis demonstrates the possibility of SAFT prediction for complex gasoline surrogates with simplified skeletal mechanisms. As the first step towards the analysis, we have compared the performance of several mechanisms from literature in predicting the laminar burning velocity and flame structure of burner stabilized 1-D flames involving TPRF mixtures. The objective behind this comparison has been to find the mechanism that provides accurate predictions in the rich side of stoichiometry for 1-D flames. The skeletal mechanisms chosen for comparison are Andrae150 (150 species and 767 reactions) from Andrae [52], Creck156 (156 species and 3370 reactions) from Creck Modelling Group [53], and LLNL312 (312 species and 2469 reactions) from Lawrence Livermore National Laboratory [51]. It may be noted here that LLNL312 has been reduced from the detailed LLNL mechanism containing 1389 species and 9604 reactions [44].

As an initial step for comparison of performance of the mechanisms, we have compared the performance of Andrae150 [52], Creck156 [53], and LLNL312 [51] with the recently published model from Atef et al. [55] and experimental data from Meng et al.[56] in predicting the laminar burning velocity of iso-octane-air mixtures. The results have been shown in Fig. A1 (Appendix). It is evident from the figure that the Creck156 [53] model provides the best performance in predicting the experimental data for rich fuel–air mixtures. Moreover, the Andrae150 [52] model also performs quite well while the Atef et al. [55] model underpredicts the laminar burning velocity in the rich side of stoichiometry.

Fig. 4 shows the comparison of performance in predicting the laminar burning velocity of TPRF surrogates with the Andrae150 [52], Creck156 [53], and LLNL312 [51] mechanisms. The experimental data are taken from Dirrenberger et al. [37] and Liao et al. [54] in Fig. 4 (a) and (b) respectively. Dirrenberger et al. [37] measured the adiabatic laminar burning velocity of TPRF surrogate (42.9 % iso-octane/13.7 % *n*-heptane/ 43.4 % toluene) at $T_{un} = 358$ K and atmospheric pressure for $\varphi = 0.6-1.5$. On the other hand, Liao et al. [54] used a TPRF composition of 69 % iso-octane/17 % *n*-heptane/14 % toluene at $T_{un} = 338$ K and atmospheric pressure for $\varphi = 0.8 - 1.3$.

As shown in Fig. 4 (a), on the lean side ($0.6 \le \phi \le 0.9$), Creck156 [53] and LLNL312 [51] mechanisms predict the laminar burning velocity more accurately than the Andrae150 [52]. However, for the rich flames ($1.1 \le \phi \le 1.4$), simulation results by Andrae150 [52] mechanism match the experimental results better with maximum deviation of around 11 % at $\phi = 1.5$. Similarly, in comparison to the experimental laminar burning velocity data by Liao et al. [54] shown in Fig. 4 (b), simulation results obtained from Creck156 [53] and LLNL312 [51] only deviate around 2 % and 5 % respectively at lean conditions. However, the Andrae150 mechanism performs significantly better at rich side of stoichiometry. Therefore, it may be concluded that among the three



Fig. 5. Major species profile distributions over the height above burner (HAB) obtained using Andrae150 (line), reduced mechanisms compared with experimental data from (a) Zeng et al. [34], (b) Wullenkord et al. [35] and (c) Dmitriev et al. [38].

skeletal mechanisms considered in this work, Andrae150 mechanism gives the most accurate laminar burning velocity prediction for TPRF flames at rich equivalence ratios.

The Andrae150 [52] has been further tested in Fig. 5 for 1-D burner stabilized flames at rich conditions. The experimental data on major

Table 1

PRF composition	s for	1-D	simulation.
-----------------	-------	-----	-------------

	1				
Fuel	Mole fraction			Blending criteria	
	C ₆ H ₅ CH ₃	i-	n-		
		C8H18	C7H16		
TPRF1	0.257	0.042	0.701	Constant C ₆ H ₅ CH ₃ volume percentage	
TPRF2	0.267	0.345	0.388		
TPRF3	0.279	0.721	0		
				· · · · · · · · · · · · · · · · · · ·	
TPRF4	0.07	0.223	0.707	Constant i-C ₈ H ₁₈ volume percentage	
TPRF5	0.2	0.216	0.584		
TPRF6	0.322	0.208	0.47		
				· · · · · · · · · · · · · · · · · · ·	
TPRF7	0.145	0.749	0.106	Constant i-C ₈ H ₁₈ /n-C ₇ H ₁₆ ratio (v/v)	
TPRF8	0.277	0.633	0.09		
TPRF9	0.397	0.528	0.075		

species profiles have been taken from Zeng et al. [34], Wullenkord et al. [35], and Dmitriev et al. [38] in Fig. 5 (a), (b), and (c) respectively. As seen from Fig. 5, in rich flames involving iso-octane ($\varphi = 1.47$), *n*-heptane ($\varphi = 1.48$), and *n*-heptane/toluene blends ($\varphi = 1.75$), species profile predictions by the Andrae150 mechanism agree well within the experimental uncertainty limit. Therefore, the Andrae150 [52] model has been used for further analysis of 1-D flames at SAFT relevant conditions in this work.

4. Results and discussions

Here, simulation results of SAFT phenomenon in both 1-D flames and well-stirred (0-D) reactor are shown and discussed. First, SAFT in 1-D TPRF flames is shown along with the brute force sensitivity analysis, reaction path analysis, and post-flame heat release analysis with a skeletally reduced mechanism [52]. The TPRF blends that show the highest amount of deviation in SAFT are identified from 1-D analysis. Then, SAFT in 0-D reactor is simulated for the TPRF blends identified from 1-D analysis with a detailed mechanism [43]. Finally, the brute force reaction sensitivity analysis results are discussed for 0-D combustion.

4.1. SAFT in 1-D flames

4.1.1. Dependence of SAFT on TPRF compositions

In this section, SAFT phenomenon in 1-D flames of i-C₈H₁₈, n-C₇H₁₆, and C₆H₅CH₃—as individual components and TPRF mixtures—in air is examined. The compositions of TPRFs are taken from Naser et al. [57]. As shown in Table 1, nine TPRF blends have been analyzed in this work. These blends are divided in three groups so that the effect of each component on SAFT can be investigated. In a recent work by Han et al. [40], SAFT in flames of i-C₈H₁₈ and n-C₇H₁₆ has been shown to occur at equivalence ratio above 1.4 only. Therefore, the present 1-D simulations have been conducted in the equivalence ratio range 1.4–2.5. The initial conditions of the flames are $T_{un} = 358$ K and P = 1 atm.

Degree of superadiabaticity (ξ_{1D}) in Fig. 6 (a-d) is calculated using equation (1) defined above. In Fig. 6 (a), ξ_{1D} in TPRF3-air is the highest throughout the studied range of equivalence ratio. At $\varphi = 2.5$ where ξ_{1D} in three TPRF mixtures reaches its maximum value, ξ_{1D} of TPRF3 flame is approximately 1.12 % and 2.57 % higher than ξ_{1D} of TPRF2 and TPRF1 flames, respectively. The gradient of ξ_{1D} with respect to φ is in the order TPRF3 > TPRF2 > TPRF1 in Fig. 6 (a). Since the amount of C₆H₅CH₃ is constant among these three surrogate mixtures and i-C₈H₁₈ increases in the order TPRF3 > TPRF2 > TPRF2 > TPRF1, it may be concluded from Fig. 6 (a) that the presence of i-C₈H₁₈ favors SAFT. In a recent study performed with CH₄/CO-air flames [58], it has been mentioned that the SAFT increases (decreases) if the amount of H is increased (decreased) in the fuel mixture. However, an opposite trend has been observed for TPRF3-air flames in Fig. 6 (a) where TPRF3 contains the lowest amount of H. Therefore, it may be concluded that the chemical reactions



Fig. 6. Simulation results of degree of superadiabaticity (ξ_{1D}) for flames of (a) TPRF-air when C₆H₅CH₃ volume percentage is constant, (b) TPRF-air when i-C₈H₁₈ volume percentage is constant, (c) TPRF-air when i-C₈H₁₈/n-C₇H₁₆ ratio (v/v) is constant, and (d) i-C₈H₁₈, n-C₇H₁₆, and C₆H₅CH₃ flames in air at $\varphi = 1.4$ –2.5, T_{un} = 358 K, and P = 1 atm.

influencing SAFT are different for different hydrocarbons.

The strong influence of i-C₈H₁₈ on SAFT can be further seen in Fig. 6 (b). Here, the volume fraction of $i-C_8H_{18}$ has been kept constant among the TPRF blends. It is evident from Fig. 6 (b) that the difference in ξ_{1D} gradient is marginal in the equivalence ratio range 1.6-2.5. To investigate the effect of C₆H₅CH₃ on SAFT, Fig. 6 (c) shows the variation of ξ_{1D} with φ for three TPRF blends (i.e., TPRF7, TPRF8, and TPRF9) with constant i-C $_8H_{18}$ /n-C $_7H_{16}$ volume fraction. It may be seen from Fig. 6 (c) that the differences in ξ_{1D} for TPRF7, TPRF8 and TPRF9 flames are considerably smaller than those for TPRFs shown in Fig. 6 (a). For example, at $\varphi = 2.5$, the gaps between ξ_{1D} in TPRF7-air flame with ξ_{1D} in TPRF8-air and TPRF9-air flames are 0.02 % and 0.01 % respectively. It is evident from Fig. 6. (a-c) that in all TPRF-air flames, SAFT starts to occur at around $\varphi = 1.6$. The degree of superadiabaticity (ξ_{1D}) in rich TPRF-air flames increases with increasing equivalence ratio. For example, the value of ξ_{1D} in flames of TPRF2-air increases by about 4.64 % as equivalence ratio rises from 1.6 to 2.5.

Finally, ξ_{1D} has been plotted for i-C₈H₁₈, n-C₇H₁₆, and C₆H₅CH₃ flames in air in Fig. 6 (d). It can be seen from the figure that the SAFT in i-C₈H₁₈-air is the highest in the range $1.6 \le \varphi \le 2.5$. At $\varphi = 2.5$, ξ_{1D} for i-C₈H₁₈ is around 3.68 % and 2.06 % higher than n-C₇H₁₆ and C₆H₅CH₃ respectively. This observation proves that i-C₈H₁₈ has the highest influence on SAFT of TPRF mixtures. In this context, it may be mentioned that the trend of SAFT—with equivalence ratio—in TPRF, i-C₈H₁₈, n-C₇H₁₆, and C₆H₅CH₃ flames is similar to the observations made by Han et al. [40,59], Sentko et al. [20], and Stelzner et al. [60] in premixed flames of C₁-C₈ hydrocarbons.

Next, to gain more insights into the nature of the growth of SAFT with the increase in i-C₈H₁₈ mole fraction, TPRF1-air, TPRF2-air, and TPRF3-air 1-D flames have been analyzed at $\varphi = 2.0$, $T_{un} = 358$ K and P



Fig. 7. Spatial distribution of flame temperature of TPRF1-air, TPRF2-air, and TPRF3-air flames at $\phi = 2.0$.

= 1 atm. As seen from the flame temperature profiles in Fig. 7, with the increase of i-C₈H₁₈ proportion from 4.2 % (TPRF1) to 72.1 % (TPRF3), the peak temperature of flame increases by 13 K while the adiabatic flame temperature decreases by around 3 K. Therefore, ξ_{1D} in the flame of TPRF3-air is larger than that of TPRF2 and TPRF1-air by around 0.5 % and 1.16 %, respectively. Based on the behaviors of flame temperature



Fig. 8. Sensitivity analysis for three flames of TPRF1-air, TPRF2-air, and TPRF3-air at $\phi = 2.0$.

that explain the increase of ξ_{1D} , the following sub-sections focus on the chemical kinetic explanations of (a) the temperature increase in the exothermic flame zone and (b) the temperature decrease in the post-flame region.

4.1.2. Sensitivity and reaction path analysis at the super adiabatic point

To investigate the chemistry behind the temperature increase in the exothermic flame zone with increasing $i-C_8H_{18}$ proportion in TPRF mixtures, brute force temperature sensitivity analysis has been performed for TPRF1-air, TPRF2-air, and TPRF3-air cases at the super adiabatic point, i.e. the location of SAFT in the flame. The sensitivity

value of every reaction (Δ_{1D}) has been calculated according to equation (3). Fig. 8 shows the results of sensitivity analysis for TPRF1-air, TPRF2-air, and TPRF3-air at $\phi = 2.0$. The inset illustrates the point in the computational domain where the analysis has been performed. It can be seen from Fig. 8 that in all three TPRF-air flames, $CO + OH = CO_2 + H$ is one of the two most influential reactions towards the temperature rise. Furthermore, the temperature sensitivity of the chain propagation reaction $CO + OH = CO_2 + H$ increases with the increase in i-C₈H₁₈ amount in the flame. Similarly, C₂H₂ + O = HCCO + H and HCCO + O₂ = CO + CO₂ + H also have large and increasing positive sensitivity to the flame temperature with the increase in i-C₈H₁₈ content.



Fig. 9. Formation route of ketenyl radical (HCCO) from iso-octane (i- C_8H_{18}) at super adiabatic point for rich ($\varphi = 2.0$) premixed TPRF-air flames.



Fig. 10. (a) Net heat release rate profiles of three studied TPRF-air flames, (b) Heat release rates of eight major endothermic reactions, R1: $C_2H_2 + HCCHCCH = C_6H_5$, R2: $H_2 + OH = H + H_2O$, R3: $H_2CCCCH (+M) = C_4H_2 + H (+M)$, R4: $CH_2 + CO (+M) = CH_2CO (+M)$, R5: $H + H_2CCCH (+M) = H_2CCCH_2 (+M)$, R6: i- $C_4H_8 = CH_2CHC.H_2 + CH_3$, R7: $H + H_3CCCH = C_2H_2 + CH_3$, and R8: $CH_3 + H (+M) = CH_4 (+M)$, at the first point of endothermic heat release region in flames of TPRF1 and TPRF3-air.

It should be noted that $C_2H_2 + O = HCCO + H$ is a chain branching reaction producing ketenyl radical (HCCO) for HCCO + $O_2 = CO + CO_2$ + H. HCCO + $O_2 = CO + CO_2 + H$ promotes the forward reaction of CO + $OH = CO_2 + H$ by producing CO that reacts with OH. As a result of this, $CO + OH = CO_2 + H$ has the highest forward reaction rate for the TPRF3 case. Other reactions contributing to flame temperature increase are the chain terminating reaction $CH_3 + H (+M) = CH_4 (+M)$ and the major branching reaction $H + O_2 = O + OH$. This is because $CH_3 + H$ $(+M) = CH_4 (+M)$ and $H + O_2 = O + OH$ consume H produced in reactions with large positive temperature sensitivity (e.g. $CO + OH = CO_2$ + H, $C_2H_2 + O = HCCO + H$, and $HCCO + O_2 = CO + CO_2 + H$). The sensitivity value of $H + O_2 = O + OH$ is the highest among positively sensitive reactions in TPRF2-air and TPRF3-air flames (Fig. 8).

It has been observed that the mole fraction of HCCO for TPRF3 surpasses that of HCCO for TPRF1 and TPRF2 at the location of maximum temperature in the flame. Considering the influence of HCCO chemistry on SAFT of TPRF surrogates, a reaction path diagram showing the formation route of HCCO from $i-C_8H_{18}$ is shown in Fig. 9. This reaction path has been generated with Cantera at the location of maximum temperature in the flame domain. It may be seen from Fig. 9 that the decomposition of iso-octyl radical (A-C_8H_{17}) to iso-butylene (IC_4H_8) and propylene (CH₂CHCH₃) is the starting point of the reaction chain that produces HCCO. Finally, HCCO is formed from $i-C_4H_3$ (H₂CCCCH)—in two different ways (a) from butatrienone (H₂C₄O) through the reaction H₂C₄O + H = C₂H₂ + HCCO and (b) through the oxidation of $i-C_4H_3$ (H₂CCCCH).

It is clear from the abovementioned sensitivity and reaction path analysis that the HCCO radical chemistry is highly influential for the SAFT in TPRF surrogate flames. While the reactions involving HCCO increase SAFT, the formation of HCCO may be traced back to the high temperature decomposition pathway of i-C₈H₁₈. Other highly influential reactions for SAFT in TPRF flames include $CO + OH = CO_2 + H$, $CH_3 + H$ (+M) = CH_4 (+M), and $H + O_2 = O + OH$.

4.1.3. Heat release analysis in the post-flame region

According to Liu et al. [17], the occurrence of temperature overshoot phenomenon is associated with the negative heat release rate in the immediate post-flame region. Total volumetric heat release rate profiles of TPRF1, TPRF2, and TPRF3-air flames are presented in Fig. 10 (a). Similar to the observation made by Liu et al. [17] for lighter hydrocarbons, the net heat release rate first increases rapidly, then drops below zero and slowly approaches equilibrium in post-flame region for all three TPRF flames in this work (Fig. 10 (a)). It can be understood that the oxidation reactions occur fast and release heat in the reaction zone (exothermicity), accompanied by heat consumption (endothermicity) of slow endothermic reactions when the system recovers to thermodynamic equilibrium.

The endothermicity starts for TPRF1, TPRF2, and TPRF3 cases at x=39.69 mm, x=39.22 mm, x=38.75 mm respectively (Fig. 10 (a) inset). At the point of peak endothermicity, around 51 % and 164 % more heat is absorbed for the TPRF3 case in comparison to TPRF2 and TPRF1, respectively. It is evident that in the flame with larger $\xi_{\rm 1D}$ (i.e. TPRF3-air case), net heat release rate decreases below zero faster (within shorter distance), reaches increasingly negative value, and takes longer to approach zero. Thus, in the post-flame region of TPRF-air flames, the endothermicity contributes to the increasing drop of temperature to its equilibrium value.

By examining the heat release rate from the individual reactions at the grid point corresponding to the start of endothermicity (as shown in the inset of Fig. 10 (a)), influential endothermic reactions for the TPRF1 and TPRF3 cases have been identified to be, R1: $C_2H_2 + HCCHCCH = C_6H_5$, R2: $H_2 + OH = H + H_2O$, R3: $H_2CCCCH (+M) = C_4H_2 + H (+M)$, R4: $CH_2 + CO (+M) = CH_2CO (+M)$, R5: $H + H_2CCCH (+M) = H_2CCCH_2 (+M)$, R6: $i-C_4H_8 = CH_2CHC.H_2 + CH_3$, R7: $H + H_3CCCH = C_2H_2 + CH_3$, and R8: $CH_3 + H (+M) = CH_4 (+M)$ (Fig. 10 (b)).

Compared to the main endothermic reactions in the post-flame region of CH₄-air flame studied in [8], there are reactions involving C3 and C4 species that affect the endothermicity of TPRF-air flames in Fig. 10 (b). It is logical since the reactions of higher hydrocarbons like toluene, n-heptane, and iso-octane promote considerable amount of C3 and C4 species in the flame. The contribution of the C3 and C4 species related reactions to the post-flame endothermicity becomes increasingly important with the increase in the mole fraction of i-C₈H₁₈ in the TPRF composition. This fact is evident from Fig. 10 (b) where C₂H₂ + HCCHCCH = C₆H₅, H₂CCCCH (+M) = C₄H₂ + H (+M), i-C₄H₈ = CH₂CHC.H₂ + CH₃, H + H₃CCCH = C₂H₂ + CH₃, and H + H₂CCCH (+M) = H₂CCCH₂ (+M) in TPRF3-air flame absorb 2.54, 2.4, 14.97, 2.22, and 2.7 times more heat than TPRF1-air flame respectively.

The chain branching reaction $i-C_4H_8 = CH_2CHC.H_2 + CH_3$ is worth pointing out as it involves a major β -scission product of iso-octane, isobutene (i-C₄H₈) [61]. Therefore, the mole fraction of i-C₄H₈ increases



Fig. 11. (a) Outlet temperature profiles of TPRF1, TPRF2, and TPRF3-air combustion at different residence times and $\phi = 2.0$ in WSR. (b) Simulation results of ξ_{0D} of TPRF1, TPRF2, and TPRF3-air combustion at $\phi = 1.5-2.5$.

considerably with the increasing i-C₈H₁₈ in the initial mixture. The increase in mole fraction of i-C₄H₈ accelerates and enhances heat absorption through i-C₄H₈ = CH₂CHC.H₂ + CH₃, which explains the relative importance of this reaction in the post-flame region. Moreover, the decomposition of i-C₄H₈ via i-C₄H₈ = CH₂CHC.H₂ + CH₃ is one of the major methyl radical (CH₃) production reactions. Hence, it promotes the recombination reaction CH₃ + H (+M) = CH₄ (+M). Besides being a significant contributor to post-flame endothermicity, CH₃ + H (+M) = CH₄ (+M) is also a significant reaction that enhances the peak flame temperature in the reaction zone (Fig. 8). Moreover, i-C₄H₈ also contributes towards the formation of HCCO in the reaction zone (Fig. 9).

The chemical pathway relevant to the endothermicity and nonequilibrium can be explained as follows,

- i-C₄H₈ = CH₂CHC.H₂ + CH₃ produces 2-propenyl (CH₂CHC.H₂), which relates to the formation of different C3 and C4 species in the TPRF-air flame.
- H consumption of CH₂CHC.H₂ via CH₂CHC.H₂ + H = H₂ + H₂CCCH₂ is a crucial reaction to the production of propadiene (H₂CCCH₂).
- H_2CCCH_2 is further isomerized to form H_3CCCH . Both H_2CCCH_2 and H_3CCCH promote substantial amount of propargyl radical (H_2CCCH), mostly via $H_2CCCH_2 + H = H_2CCCH + H_2$ and $H_3CCCH + H = H_2CCCH + H_2$.
- The increase of C_2H_2 mole fraction throughout the post-flame region in TPRF3-air flame is explained by the influence of H_3 CCCH on the production C_2H_2 via $H + H_3$ CCCH = $C_2H_2 + CH_3$. The increasing amount of C_2H_2 in post-flame region accounts for the increasing influence of $C_2H_2 + HCCHCCH = C_6H_5$ among the major endothermic reactions.
- Reaction $H_2CCCH + H = C_3H_2 + H_2$ is the major propadienylidene radical (C_3H_2) production reaction.
- $C_3H_2 + CH_3 = CH_2CHCCH + H$ produces vinyl acetylene (CH₂CHCCH).
- H abstraction through CH₂CHCCH + H = H₂CCCCH + H₂ of vinyl acetylene (CH₂CHCCH), is responsible for the production of 1-butene-3-yne-2-yl radical (H₂CCCCH).

The above-mentioned reaction pathway explains the increase in the amount of i-C₄H₈, CH₂CHC.H₂, H₂CCCH₂, H₃CCCH, H₂CCCH, C₃H₂, CH₂CHCCH, and H₂CCCCH in the flame with larger mole fraction of i-C₈H₁₈. Mole fraction of these C3 and C4 radicals and species also remain high and well above equilibrium amount in the post-flame region. Therefore, the relative significance to the heat absorption and the delay to equilibrium of endothermic reactions involving these species

increases in TPRF3-air flame compared to TPRF2-air and TPRF1-air flames.

The above discussion leads to the conclusion that the advanced decomposition of i-C₄H₈ via i-C₄H₈ = CH₂CHC.H₂ + CH₃ affects the amount of certain C3, C4 species and C₂H₂, thus being responsible for the increased endothermicity. This translates to the increasing yet slower drop of temperature to its equilibrium value in the post-flame region of the flame having higher i-C₈H₁₈. The enhanced temperature rise in the reaction zone due to the reactions shown in Fig. 8 combined with the temperature decline in post-flame region due to the endothermic reactions shown in Fig. 10 (b) cause the increase in degree of SAFT (ξ_{1D}) in TPRF-air flames with more i-C₈H₁₈ in the composition.

4.2. SAFT in 0-D reactor

The previous section employs a skeletal mechanism from Andrae [52] for analysis of SAFT in nine TPRF blends. In order to gain more indepth understanding of SAFT in TPRF-air flames, 0-D analysis with one of the most recent gasoline surrogate mechanisms [43] has been performed in this section. It has been observed from results shown in Fig. 6 (a) that the flames of TPRF1, TPRF2 and TPRF3-air show a clear difference in the ξ_{1D} . Thus, these three surrogate compositions (Table 1) are selected for the 0-D analysis. Similar to the 1-D analysis, the initial pressure and temperature conditions for the 0-D simulations are $T_{un} = 358$ K and P = 1 atm. The equivalence ratio range for 0-D simulation of TPRF-air is between 1.5 and 2.5.

The temperatures from the WSR simulations are plotted with varied residence times (τ_{res}) in Fig. 11 (a) at equivalence ratio 2.0. It can be seen from the figure that the reactor temperature increases in the range 619 \times 10⁻⁵ s $\leq \tau_{res} \leq$ 721 \times 10⁻⁴ s. After the increase, the temperature starts to decrease—beyond $\tau_{res} = 721 \times 10^{-4}$ s—and approaches equilibrium value at sufficiently large residence time. Therefore, the initial increase in WSR temperature with τ_{res} may be attributed to the occurrence of super equilibrium [9]. The peak reactor temperature $(T_{WSR,peak})$ over a large span of residence time (619 \times 10⁻⁵ s \leq $\tau_{res} \leq$ 4 s) has been calculated for different equivalence ratios. This way, the non-dimensional degree of SAFT (ξ_{0D}), obtained using equation (2), has been shown in Fig. 11 (b). As can be seen from Fig. 11 (b), SAFT is observed in all three TPRF-air flames, starting at $\varphi \sim 1.7$. As the equivalence ratio increases, ξ_{0D} also increases. For example, ξ_{0D} in three studied TPRF-air mixtures at $\varphi = 2.5$ increases by around 22–25 % compared to ξ_{0D} at $\varphi = 1.7$. Similar to ξ_{1D} in Fig. 6 (a), the TPRF3-air flames always have the highest ξ_{0D} , while ξ_{0D} for TPRF1-air case are the lowest in Fig. 11 (b). Since TPRF3 contains the highest amount of $i-C_8H_{18}$ (Table 1), it may be concluded



Fig. 12. Sensitivity analysis for 0-D combustion of TPRF1, TPRF2, and TPRF3 in air at $\varphi = 2.0$.

that i-C $_8H_{18}$ influences SAFT in 0-D TPRF-air combustion as well.

Next, sensitivity analysis—at τ_{res} corresponding to $T_{WSR,peak}$ for $\varphi = 2.0$ (inset of Fig. 12)—has been performed with the detailed C3MechV3.3 [43] to study the effect of chemical kinetics on the increase of WSR temperature. The results of the sensitivity analysis are shown in Fig. 12. According to equation (2), increase in the maximum outlet temperature ($T_{WSR,peak}$) at a certain residence time by an accelerated reaction indicates higher degree of SAFT in WSR (ξ_{OD}).

It may be seen from Fig. 12, that the highest positive sensitivity value occurs for the chain branching reaction $H + O_2 = O + OH$ in the three TPRF-air flames. The positive influence of $H + O_2 = O + OH$ on temperature is attributed to its contribution to increasing active radicals, thus increasing reactivity of the mixture in the WSR. Three-body terminating reaction $CH_3 + H (+M) = CH_4 (+M)$ also has high positive sensitivity to the temperature. Two reactions involving abstraction of H from propargyl radical ($C_3H_3 + H = C_3H_4$ -P and $C_3H_3 + H = C_3H_4$ -A) are among major reactions having positive sensitivity values. It is worth pointing out that all reactions promoting the increase in reactor temperature shown in Fig. 12 are H consumption reactions, among which $H + O_2 = O + OH$ and $CH_3 + H (+M) = CH_4 (+M)$ are more substantial. It is similar to the effects of these two reactions in temperature sensitivity analysis of 1-D flames as main H consumption reactions and two of the most influential reactions towards the temperature rise (Fig. 8).

In case of $C_2H_5 + H = 2$ CH₃, sensitivity analysis shows that the forward reaction has potential to decrease the temperature. However, it has been found that $C_2H_5 + H = 2$ CH₃ is progressing in reverse direction in the flame. Therefore, its contribution is to increase the temperature. Similar to the 1-D flame, CO + OH = CO₂ + H also has quite high temperature sensitivity value and large reaction rate proceeding in forward direction. Therefore, it may be understood that the forward reaction of CO + OH = CO₂ + H and reverse reaction of $C_2H_5 + H = 2$ CH₃ promote the increase in WSR temperature by producing H radicals, that are consumed by other (positively sensitive) reactions. The contributions of H consumption reactions (for example, H + O₂ = O + OH, CH₃ + H (+M) = CH₄ (+M), C₃H₃ + H = C₃H₄-A, and C₃H₃ + H = C₃H₄-A) are very important to the temperature rise and the degree of SAFT. It

has been observed in this study that TPRF1 generates lower amount of H radicals in comparison to TPRF2 and TPRF3. Therefore, the SAFT is also lower for TPRF1 due to the above-mentioned reaction mechanism.

It has been found in this work that the degree of SAFT in both 1-D flame (ξ_{1D}) and 0-D reactor (ξ_{0D}) simulations relates to H and OH consumption reactions. The relation between increasing consumption of H and increasing degree of SAFT shows similarities with the conclusion drawn by Liu and Gülder [8] that the fundamental cause of SAFT in rich hydrocarbon flames is the relative scarcity of H radical. On the other hand, for 1-D flames, temperature sensitive reactions also involve the production and consumption of HCCO. Reactions of C3 species are influential to the degree of SAFT in both 1-D and 0-D cases through different ways. Based on heat release analysis for 1-D flames, those reactions (e.g. $H + H_2CCCH (+M) = H_2CCCH_2 (+M)$ and $H + H_3CCCH =$ $C_2H_2 + CH_3$) are among important endothermic reactions in the postflame region that contribute to the increasing drop of flame temperature to the adiabatic equilibrium temperature. While in 0-D reactor, sensitivity analysis indicates that the role of reactions such as $C_3H_3 + H$ $= C_3H_4$ -P and $C_3H_3 + H = C_3H_4$ -A is to increase the outlet temperature at a certain residence time compared to the equilibrium value. Therefore, it may be concluded that (a) 0-D reactor temperature sensitivity analysis with detailed mechanism can point out the relevant chemical routes for SAFT in gasoline-air flames and (b) for the 1-D analysis with validated skeletal mechanisms, both temperature sensitivity analysis in the flame zone and heat release analysis in the post-flame region are needed for complete understanding of SAFT in premixed TPRF-air flames.

5. Conclusions

In the present work, the super adiabatic flame temperature (SAFT) phenomenon has been studied numerically for 1-D and 0-D combustion of toluene primary fuels (TPRF) in air. Non-dimensional parameters ξ_{1D} and ξ_{0D} were defined to measure the degree of superadiabaticity in 1-D flames and well-stirred (0-D) reactor, respectively. The chemical kinetic characteristics of SAFT were investigated with brute force type temperature sensitivity analysis (for 1-D and 0-D cases) and post-flame heat

release analysis (for 1-D case). Main findings are summarized as follows:

- 1. Super adiabatic equilibrium temperature has been found in 1-D flames and 0-D reactors of TPRF-air with equivalence ratio $\varphi \ge$ 1.6 and $\varphi \ge$ 1.7, respectively. The degree of SAFT (ξ_{1D} and ξ_{0D}) rises remarkably with increasing equivalence ratio. At the same initial conditions (unburnt gas temperature, pressure, and equivalence ratio), ξ_{1D} and ξ_{0D} increase as the mole fraction of iso-octane increases in the TPRF surrogate mixtures. The mole fraction of toluene and *n*-heptane do not affect the magnitude of SAFT to a great extent.
- 2. It has been observed in 1-D flames of TPRF-air that the peak flame temperature rises with increasing iso-octane proportion. The temperature increase in the reaction zone is followed by the larger endothermicity in the post-flame region, causing the increase in ξ_{1D} . The temperature increase in exothermic flame zone and temperature decrease in post-flame region have been analyzed separately. Major findings from this analysis are:
- (a) Temperature sensitivity and reaction path analysis in fuel-rich TPRF-air 1-D flames indicate that reactions involving production and consumption of HCCO ($C_2H_2 + O = HCCO + H$, HCCO + $O_2 = CO + CO_2 + H$, and $CO + OH = CO_2 + H$) promote the increase in flame temperature in the reaction zone. Moreover, HCCO is generated from the β -scission products of iso-octyl radical. Some H consumption reactions such as $CH_3 + H$ (+M) = CH_4 (+M) and $H + O_2 = O + OH$ are among positively sensitive reactions to the flame temperature also.
- (b) Post-flame heat release analysis shows that the endothermic reactions cause delay to reach equilibrium state in the post-flame region. Iso-octane augments such delays as the unimolecular decomposition of a β -scission product of iso-octane, i.e., iso-butene (i-C₄H₈) through i-C₄H₈ = CH₂CHC.H₂ + CH₃, is highly endothermic.
- (c) Moreover, different C3, C4 species, and C₂H₂ are formed from isobutene. Therefore, the relative importance of endothermic reactions involving these smaller molecules also increases with increased iso-octane in TPRF.
- 3. In 0-D reactor, H consumption reactions like $H + O_2 = O + OH$, $CH_3 + H (+M) = CH_4 (+M)$, $C_3H_3 + H = C_3H_4$ -A, and $C_3H_3 + H = C_3H_4$ -A are more influential to the temperature rise and to the degree of SAFT than other H production reactions like CO + OH $= CO_2 + H$ and $2 CH_3 = C_2H_5 + H$.
- 4. The common observation for both 1-D flame and 0-D reactor of TPRF combustion with air is the correlation between H and OH consumption reactions and increasing degree of SAFT. Moreover, 0-D analysis presents the effects of C3 species on the increase in reactor outlet temperature and 1-D analysis shows that C3 species influence the decrease of flame temperature to adiabatic equilibrium value in the post-flame region.

The experimental determination of SAFT in gasoline surrogates is a future scope of research. As the simulations using skeletal mechanism can also provide useful insights of SAFT, the present study suggests that dedicated skeletal mechanisms can be developed for SAFT analysis of gasoline/biofuel blends in future.

CRediT authorship contribution statement

Giang Bui: Conceptualization, Methodology, Software, Validation, Formal analysis, Writing – original draft, Visualization. Atmadeep Bhattacharya: Conceptualization, Methodology, Software, Validation, Writing – review & editing, Funding acquisition. Ossi Kaario: Supervision, Writing – review & editing, Project administration. Ville Vuorinen: Supervision, Funding acquisition. Rupali Tripathi: Conceptualization, Writing – review & editing. Teemu Sarjovaara: Writing – review & editing, Project administration.



Fig. A1. Laminar burning velocity of iso-octane-air mixture obtained using Atef et al. (green dash-dot line) [55], Andrae150 (black solid line) [52], Creck156 (red dashed line) [53], and LLNL312 (blue dot line) [51] mechanisms compared with experimental data from Meng et al. [56]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix

References

- EIA. International Energy Outlook 2016 With Projections to 2040. 2016. https:// doi.org/DOE/EIA-0383(2013).
- [2] EIA. International Energy Outlook 2019. US Energy Inf Adm 2019;September: 25–150.
- [3] Heywood JB. Internal Combustion Engine Fundementals. vol. 21. 1988.
- [4] Storch M, Hinrichsen F, Wensing M, Will S, Zigan L. The effect of ethanol blending on mixture formation, combustion and soot emission studied in an optical DISI engine. Appl Energy 2015;156:783–92. https://doi.org/10.1016/j. appenergy.2015.06.030.
- [5] Konnov AA, Mohammad A, Kishore VR, Il KN, Prathap C, Kumar S. A comprehensive review of measurements and data analysis of laminar burning velocities for various fuel+air mixtures. Prog Energy Combust Sci 2018;68: 197–267. https://doi.org/10.1016/j.pecs.2018.05.003.
- [6] Chen Z. On the accuracy of laminar flame speeds measured from outwardly propagating spherical flames: Methane/air at normal temperature and pressure. Combust Flame 2015;162:2442–53. https://doi.org/10.1016/j. combustflame.2015.02.012.
- [7] Faghih M, Chen Z, Huo J, Ren Z, Law CK. On the determination of laminar flame speed from low-pressure and super-adiabatic propagating spherical flames. Proc Combust Inst 2019;37:1505–12. https://doi.org/10.1016/j.proci.2018.05.027.

- [8] Liu F, Gülder ÖL. Effects of H2 and H preferential diffusion and unity Lewis number on superadiabatic flame temperatures in rich premixed methane flames. Combust Flame 2005;143:264–81. https://doi.org/10.1016/j.combustflame.2005.03.018.
- Meeks E, Kee RJ, Dandy DS, Coltrin ME. Computational simulation of diamond chemical vapor deposition in premixed C2H2/O2/H2 and CH4O2-strained flames. Combust Flame 1993;92:144–60. https://doi.org/10.1016/0010-2180(93)90204-G.
- [10] Korobeinichev OP, Paletsky AA, Bolshova TA, Knyazev VD. A numerical study of the superadiabatic flame temperature phenomenon in HN 3 flames. Combust Theory Model 2012;16:927–39. https://doi.org/10.1080/13647830.2012.687458.
- [11] Babkin VS, Bunev VA, Bolshova TA. Superadiabatic temperature phenomenon in the combustion processes due to a competition between chemical reactions. Combust Explos Shock Waves 2015;51:151–9. https://doi.org/10.1134/ S0010508215020021.
- [12] Bertagnolli KE, Lucht RP. Temperature profile measurements in stagnation-flow, diamond-forming flames using hydrogen cars spectroscopy. Symp Combust 1996; 26:1825–33. https://doi.org/10.1016/S0082-0784(96)80003-8.
- [13] Ruf B, Behrendt F, Deutschmann O, Kleditzsch S, Warnatz J. Modeling of chemical vapor deposition of diamond films from acetylene-oxygen flames. Proc Combust Inst 2000;28:1455–61. https://doi.org/10.1016/S0082-0784(00)80362-8.
- [14] Takagi T, Xu Z. Numerical analysis of laminar diffusion flames—Effects of preferential diffusion of heat and species. Combust Flame 1994;96:50–9. https:// doi.org/10.1016/0010-2180(94)90157-0.
- [15] Zamashchikov VV, Namyatov IG, Bunev VA, Babkin VS. On the Nature of Superadiabatic Temperatures in Premixed Rich Hydrocarbon Flames. Combust Explos Shock Waves 2004;40:32–5. https://doi.org/10.1023/B: CESW.0000013665.43183.10.
- [16] Bunev VA, Babkin VS. Chemical reactions in the low-temperature zone of a laminar rich propane-air flame. Combust Explos Shock Waves 2006;42:503–8. https://doi. org/10.1007/S10573-006-0082-Y.
- [17] Liu F, Guo H, Smallwood GJ, Gülder ÖL. Numerical study of the superadiabatic flame temperature phenomenon in hydrocarbon premixed flames. Proc Combust Inst 2002;29:1543–50. https://doi.org/10.1016/S1540-7489(02)80189-4.
- [18] Liu F, Gülder ÖL. Effects of pressure and preheat on super-adiabatic flame temperatures in rich premixed methane/air flames. Combust Sci Technol 2008; 180:437–52. https://doi.org/10.1080/00102200701741285.
- [19] Wang Y, Chen X, Chen Z. Super-adiabatic temperature in homogenous ignition of CH4/O2/N2 mixtures. Fuel 2022;319:123854. https://doi.org/10.1016/j. fuel.2022.123854.
- [20] Sentko MM, Schulz S, Stelzner B, Anderlohr C, Vicari M, Trimis D. Determination of temperature and water-concentration in fuel-rich oxy-fuel methane flames applying TDLAS. Combust Flame 2020;214:336–45. https://doi.org/10.1016/j. combustflame.2020.01.003.
- [21] Sentko MM, Schulz S, Stelzner B, Anderlohr C, Vicari M, Trimis D. Experimental investigation of the pressure influence on flame structure of fuel-rich oxy-fuel methane flames for synthesis gas production. Fuel 2021;286:119377. https://doi. org/10.1016/j.fuel.2020.119377.
- [22] Han X, Wang Z, He Y, Liu Y, Zhu Y, Konnov AA. The temperature dependence of the laminar burning velocity and superadiabatic flame temperature phenomenon for NH3/air flames. Combust Flame 2020;217:314–20. https://doi.org/10.1016/j. combustflame.2020.04.013.
- [23] Pitz WJ, Cernansky NP, Dryer FL, Egolfopoulos FN, Farrell JT, Friend DG, et al. Development of an experimental database and chemical kinetic models for surrogate gasoline fuels. SAE Tech Pap 2007. https://doi.org/10.4271/2007-01-0175.
- [24] Sarathy SM, Farooq A, Kalghatgi GT. Recent progress in gasoline surrogate fuels. Prog Energy Combust Sci 2018;65:67–108. https://doi.org/10.1016/j. pecs.2017.09.004.
- [25] Bhattacharya A. Analysis of laminar premixed flame structure of isooctane / 2methylfuran / air mixtures with a skeletal mechanism 2021. https://doi.org/ 10.1080/13647830.2021.1970231.
- [26] Bhattacharya A, Banerjee DK, Mamaikin D, Datta A, Wensing M. Effects of Exhaust Gas Dilution on the Laminar Burning Velocity of Real-World Gasoline Fuel Flame in Air. Energy Fuel 2015;29:6768–79. https://doi.org/10.1021/acs. energyfuels.5b01299.
- [27] Bhattacharya A, Shahanaghi A, Kaario O, Vuorinen V, Tripathi R, Sarjovaara T. Effects of blending 2,5-dimethylfuran and dimethyl ether to toluene primary reference fuels: A chemical kinetic study. Fuel 2021;304:121401. https://doi.org/ 10.1016/j.fuel.2021.121401.
- [28] Bhattacharya A, Kaario O, Vuorinen V, Tripathi R, Sarjovaara T. Analysis of Gasoline Surrogate Combustion Chemistry with a Skeletal Mechanism. SAE Tech. Pap. 2020-01-2004, SAE International; 2020.
- [29] Sarathy SM, Kukkadapu G, Mehl M, Wang W, Javed T, Park S, et al. Ignition of alkane-rich FACE gasoline fuels and their surrogate mixtures. Proc Combust Inst 2015. https://doi.org/10.1016/j.proci.2014.05.122.
- [30] Douté C, Delfau JL, Akrich R, Vovelle C. Experimental study of the chemical structure of low-pressure premixed n-heptane-O2-Ar and iso-octane-O2-Ar flames. Combust Sci Technol 1997;124:249–76. https://doi.org/10.1080/ 00102209708935647.
- [31] Bakali AE, Delfau JL, Vovelle C. Experimental Study of 1 Atmosphere, Rich, Premixed n-heptane and iso-octane Flames. Combust Sci Technol 1998;140:69–91. https://doi.org/10.1080/00102209808915768.
- [32] Li Y, Huang C, Wei L, Yang B, Wang J, Tian Z, et al. An experimental study of rich premixed gasoline/O2/Ar flame with tunable synchrotron vacuum ultraviolet photoionization. Energy Fuel 2007;21:1931–41. https://doi.org/10.1021/ ef0700578.

- [33] Li Y, Cai J, Zhang L, Qi F. Kinetic modeling study of fuel-rich premixed toluene flame at low pressure. Lixue Xuebao/Chinese J Theor Appl Mech 2010;42:607–14.
- [34] Zeng M, Wullenkord J, Graf I, Kohse-Höinghaus K. Influence of dimethyl ether and diethyl ether addition on the flame structure and pollutant formation in premixed iso-octane flames. Combust Flame 2017;184:41–54. https://doi.org/10.1016/j. combustflame.2017.05.028.
- [35] Wullenkord J, Graf I, Baroncelli M, Felsmann D, Cai L, Pitsch H, et al. Laminar premixed and non-premixed flame investigation on the influence of dimethyl ether addition on n-heptane combustion. Combust Flame 2020;212:323–36. https://doi. org/10.1016/j.combustflame.2019.11.012.
- [36] Osipova KN, Bolshova TA, Korobeinichev OP, Kuibida LV, Shmakov AG. Effect of Addition of Methyl Hexanoate and Ethyl Pentanoate on the Structure of Premixed n-Heptane/Toluene/O2/Ar Flame. Energy Fuel 2019;33:4585–97. https://doi.org/ 10.1021/acs.energyfuels.9b00166.
- [37] Dirrenberger P, Glaude PA, Bounaceur R, Le GH, Pires A, Konnov AA, et al. Laminar burning velocity of gasolines with addition of ethanol. Fuel 2014;115: 162–9. https://doi.org/10.1016/j.fuel.2013.07.015.
- [38] Dmitriev AM, Knyazkov DA, Bolshova TA, Shmakov AG, Korobeinichev OP. The effect of methyl pentanoate addition on the structure of premixed fuel-rich nheptane/toluene flame at atmospheric pressure. Combust Flame 2015;162: 1964–75. https://doi.org/10.1016/j.combustflame.2014.12.015.
- [39] Zhang Y, Jiao A, Li Y, Liu P, Yang G, Zhan R, et al. Chemical effects of anisole and toluene addition to n-heptane on PAH characteristics in laminar premixed flames by LIF measurement and kinetic model. Fuel 2021:303. https://doi.org/10.1016/j. fuel.2021.121255.
- [40] Han X, Wang Z, He Y, Wang S, Liu Y, Konnov AA. Temperature dependence of the laminar burning velocity for n-heptane and iso-octane/air flames. Fuel 2020;276: 1–10. https://doi.org/10.1016/j.fuel.2020.118007.
- [41] David G. Goodwin, Raymond L. Speth, Harry K. Moffat and BWW. Cantera: An object-oriented software toolkit for chemical kinetics, thermodynamics, and transport processes. 2021. https://doi.org/10.5281/zenodo.4527812.
- [42] Turns SR. An introduction to combustion: concepts and applications. 2nd ed. McGraw-Hill Education; 2000.
- [43] Dong S, Wagnon SW, Pratali Maffei L, Kukkadapu G, Nobili A, Mao Q, et al. A new detailed kinetic model for surrogate fuels: C3MechV3.3. Appl Energy Combust Sci 2022;9:100043. https://doi.org/10.1016/j.jaecs.2021.100043.
- [44] Mehl M, Pitz WJ, Westbrook CK, Curran HJ. Kinetic modeling of gasoline surrogate components and mixtures under engine conditions. Proc Combust Inst 2011;33: 193–200. https://doi.org/10.1016/j.proci.2010.05.027.
- [45] Fang R, Saggese C, Wagnon SW, Sahu AB, Curran HJ, Pitz WJ, et al. Effect of nitric oxide and exhaust gases on gasoline surrogate autoignition: iso-octane experiments and modeling. Combust Flame 2022;236:111807. https://doi.org/10.1016/j. combustflame.2021.111807.
- [46] Shao C, Wang H, Atef N, Wang Z, Chen B, Almalki M, et al. Polycyclic aromatic hydrocarbons in pyrolysis of gasoline surrogates (n-heptane/iso-octane/toluene). Proc Combust Inst 2019;37:993–1001. https://doi.org/10.1016/j. proci.2018.06.087.
- [47] Chen B, Togbé C, Wang Z, Dagaut P, Sarathy SM. Jet-stirred reactor oxidation of alkane-rich FACE gasoline fuels. Proc Combust Inst 2017;36:517–24. https://doi. org/10.1016/j.proci.2016.05.040.
- [48] Chen B, Togbé C, Selim H, Dagaut P, Sarathy SM. Quantities of Interest in Jet Stirred Reactor Oxidation of a High-Octane Gasoline. Energy Fuel 2017;31: 5543–53. https://doi.org/10.1021/acs.energyfuels.6b03193.
- [49] Badra J, AlRamadan AS, Sarathy SM. Optimization of the octane response of gasoline/ethanol blends. Appl Energy 2017;203:778–93. https://doi.org/10.1016/ j.apenergy.2017.06.084.
- [50] Dagaut P, Karsenty F, Dayma G, Diévart P, Hadj-Ali K, Mzé-Ahmed A, et al. Experimental and detailed kinetic model for the oxidation of a Gas to Liquid (GtL) jet fuel. Combust Flame 2014;161:835–47. https://doi.org/10.1016/j. combustflame.2013.08.015.
- [51] Mehl M, Chen JY, Pitz WJ, Sarathy SM, Westbrook CK. An approach for formulating surrogates for gasoline with application toward a reduced surrogate mechanism for CFD engine modeling. Energy Fuel 2011. https://doi.org/10.1021/ ef201099y.
- [52] Andrae JCG. A kinetic modeling study of self-ignition of low alkylbenzenes at engine-relevant conditions. Fuel Process Technol 2011;92:2030–40. https://doi. org/10.1016/j.fuproc.2011.06.004.
- [53] Ranzi E, Frassoldati A, Stagni A, Pelucchi M, Cuoci A, Faravelli T. Reduced kinetic schemes of complex reaction systems: Fossil and biomass-derived transportation fuels. Int J Chem Kinet 2014;46:512–42. https://doi.org/10.1002/kin.20867.
 [54] Liao YH, Roberts WL. Laminar Flame Speeds of Gasoline Surrogates Measured with
- [54] Liao YH, Roberts WL. Laminar Flame Speeds of Gasoline Surrogates Measured with the Flat Flame Method. Energy Fuel 2016;30:1317–24. https://doi.org/10.1021/ acs.energyfuels.5b01433.
- [55] Atef N, Kukkadapu G, Mohamed SY, Al RM, Banyon C, Mehl M, et al. A comprehensive iso-octane combustion model with improved thermochemistry and chemical kinetics. Combust Flame 2017;178:111–34. https://doi.org/ 10.1016/j.combustflame.2016.12.029.
- [56] Meng Z, Liang K, Fang J. Laminar burning velocities of iso-octane, toluene, 1hexene, ethanol and their quaternary blends at elevated temperatures and pressures. Fuel 2019;237:630–6. https://doi.org/10.1016/j.fuel.2018.10.072.
- [57] Naser N, Sarathy SM, Chung SH. Estimating fuel octane numbers from homogeneous gas-phase ignition delay times. Combust Flame 2018;188:307–23. https://doi.org/10.1016/j.combustflame.2017.09.037.
- [58] Shvartsberg VM, Bunev VA. Synergistic Effects in Flames of Mixtures of Methane and Carbon Monoxide with Air. Combust Explos Shock Waves 2021;57:511–20. https://doi.org/10.1134/s0010508221050014.

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- [59] Han X, Wang Z, He Y, Wang S, Zhu Y, Konnov AA. Over-rich combustion of CH4, C2H6, and C3H8 +air premixed flames investigated by the heat flux method and kinetic modeling. Combust Flame 2019;210:339–49. https://doi.org/10.1016/j. combustflame.2019.09.009.
- [60] Stelzner B, Weis C, Habisreuther P, Zarzalis N, Trimis D. Super-adiabatic flame temperatures in premixed methane flames: A comparison between oxy-fuel and

conventional air combustion. Fuel 2017;201:148–55. https://doi.org/10.1016/j. fuel.2017.01.025.

 [61] Davis SG, Law CK. Laminar flame speeds and oxidation kinetics of iso-octane-air and n-heptane-air flames. Symp Combust 1998;27:521–7. https://doi.org/ 10.1016/S0082-0784(98)80442-6.