Three-stage heat release in n-heptane auto-ignition

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Abstract

Multi-stage heat release is an important feature of hydrocarbon auto-ignition that influences engine operation. This work presents findings of previously unreported three-stage heat release in the auto-ignition of n-heptane/air mixtures at lean equivalence ratios and high pressures. Detailed homogenous gas-phase chemical kinetic simulations were utilized to identify conditions where two-stage and three-stage heat release exist. Temperature and heat release profiles of lean n-heptane/air auto-ignition display three distinct stages of heat release, which is notably different than two-stage heat release typically reported for stoichiometric fuel/air mixtures. Concentration profiles of key radicals (HO_2 and OH) and intermediate/product species (CO and CO_2) also display unique behavior in the lean auto-ignition case. Rapid compression machine measurements were performed at a lean equivalence ratio to confirm the existence of three-stage heat release in experiments. Laser diagnostic measurements of CO concentrations in the RCM indicate similar concentration-time profiles as those predicted by kinetic modeling. Computational singular perturbation was then used to identify key reactions and species contributing to explosive time scales at various points of the three-stage ignition process. Comparisons with two-stage ignition at stoichiometric conditions indicate that thermal runaway at the second stage of heat release is inhibited under lean conditions. $\text{H} + \text{O}_2$ chain branching and CO oxidation reactions drive high-temperature heat release under stoichiometric conditions, but these reactions are suppressed by H , OH , and HO_2 radical termination reactions at lean conditions, leading to a distinct third stage of heat release.

Keywords: chemical kinetics modeling, hydrocarbon ignition, auto-oxidation, multi-stage ignition, computational singular perturbation, rapid compression machine

1. Introduction

Fuel/air auto-ignition is a critical combustion property governing the operation of engines. Auto-ignition determines the knock limits of spark ignition engines [1] and the efficiency and emissions of compression ignition engines [2]. Aero-engines and stationary power generation turbines control auto-ignition for safety reasons and/or to extend operability limits [3]. This work aims to provide new insights into the ignition characteristics of n-heptane, a widely used surrogate molecule for studying combustion of practical hydrocarbon fuels [4,5].

n-Heptane oxidation has been studied extensively, as recently summarized by [3,6,7]. The auto-ignition kinetics of n-heptane, and other n-alkanes, in practical engines has been adequately discussed by Westbrook et al. [8]. Briefly, hydrocarbon auto-ignition at high temperatures is governed by reactions between atomic hydrogen with molecular oxygen, while hydrogen peroxide (H_2O_2) decomposition drives auto-ignition at intermediate temperatures. Complex low-temperature termination, propagation, and branching pathways forming alkenes, cyclic ethers, and keto-hydroperoxides (KHP) [9,10], respectively, control heat release rate, raise system temperature, and advance formation and decomposition of H_2O_2 . The chemical kinetics of low-temperature oxidation [11] is strongly related to fuel molecular structure, and can be linked to interesting combustion phenomena such as cool flames [12], negative temperature coefficient (NTC) behavior [13], and fuel anti-knock quality (i.e., octane numbers) [14].

Two-stage heat release is a feature of alkane auto-ignition [15-17] that has attracted significant research interest in both fundamental [18] and practical [19] applications. This phenomenon is characterized by a low-temperature heat release (LTHR) regime that raises the system temperature and results in the first stage (τ_1) ignition delay time (IDT). LTHR is driven by chain branching auto-oxidation reactions that result in the formation and decomposition of highly oxygenated intermediates (e.g., ketohydroperoxides) [20]. LTHR is followed by a net decrease in the net heat release rate (HRR)

due to NTC chemistry [20]; subsequent transition to high-temperature heat release (HTHR) results in the total (τ_T) IDT, which is characterized by H_2O_2 decomposition, $H+O_2$ chain branching, and CO oxidation reactions.

Auto-ignition phenomena with more than two stages of heat release have been seldom reported in the literature. Intermediate-temperature heat release (ITHR) has been observed in engines [19,21,22]; however, this is not a distinct stage of heat release because it is typically merged with the HTHR and the controlling chemistry is attributed to traditional competition between alkyl peroxy radical chain branching, propagation, and termination pathways. Yamamoto et al. [23] reported three-stage oxidation of n-heptane/air in a micro-flow reactor with controlled temperature profile. Their experiments and simulations highlighted the effect of pressure on the three stages of heat release.

This work explores multi-stage heat release in n-heptane/air auto-ignition using detailed chemical kinetic simulations. Three stages of heat release are identified at lean conditions, high pressures, and low-to-intermediate temperatures. Intermediate species' concentration profiles indicate that the chemistry of three-stage heat release is notably different than that of single- and two-stage heat release, most notably carbon monoxide (CO) formation and consumption profiles. Rapid compression machine (RCM) experiments demonstrate that three-stage heat release is present under specific operating regimes, and laser diagnostics shows similar CO oxidation behavior as predicted numerically. Finally, computational singular perturbation (CSP) analysis elucidates the underlying chemical kinetic phenomenon responsible for three-stage heat release and its distinguishing features compared to two-stage heat release.

2. Experimental and Computational Methods

2.1. Chemical kinetic modeling

The auto-ignition of n-heptane/air mixtures was simulated in both constant volume and constant pressure batch reactor simulations using the detailed chemical kinetic model developed by Zhang et al. [6] in CHEMKIN PRO [24]. Additional simulations were performed in Cantera [25] and OpenSMOKE++ [26], both implemented in CloudFlame [27], as well as with n-heptane kinetic models from Cai et al. [28] and Pelucchi et al. [29]. The simulations spanned pressures from 10 to 60 atm, temperatures from 500 to 1200 K, and equivalence ratios from 0.3 to 1.0. In simulations showing two-stage heat release and three-stage heat release, τ_1 , τ_2 , and τ_T were defined as the time corresponding to maximum heat release rate in each regime.

2.2. RCM experiments

Experiments were conducted in the RCM facility at KAUST with lean n-heptane/air gas mixtures to observe potential indications of three-stage ignition. Details of this RCM can be found in previous works [30,31]. The KAUST RCM has a dual piston design with six ports available in the center of the combustion chamber for implementing sensors. Time-resolved pressure profile was measured using a Kistler 6045A pressure transducer. Additionally, two of the ports were fitted with sapphire windows to provide optical access for laser absorption measurements. The test gas mixture is assumed to be homogeneous. The laser system implemented in this work is similar to the one in [30] with the difference being that instead of two quantum cascade lasers, only one laser at 4.89 μm was used to quantify CO mole fraction with an experimental uncertainty of 5%. The Beer-Lambert relation was used to convert measured absorbance profiles to CO mole fraction (X_{CO}) profiles with spectroscopic parameters taken from the HITRAN database[32]. Post-compression temperature profile was inferred from the measured pressure, P , using the isentropic gas relation [30].

Experimental conditions in RCM experiments are typically chosen such that the first-stage ignition delay is at least 3 ms after the end-of-compression (EOC) to minimize reactivity during the compression stage. However, in the interest of observing three-stage ignition behavior, certain EOC conditions were chosen wherein first-stage heat release occurs shortly after EOC. Experiments were conducted at compressed pressure of 20 atm, equivalence ratio of 0.3, and compressed temperatures ranging 700 to 900 K.

2.3. Computational Singular Perturbation (CSP) Tools

CSP is an algorithmic method of asymptotic analysis that has been widely used for the investigation of various combustion processes. The reader is referred to [33] for a more detailed description of the method. In the current study, tools generated on the basis of CSP, were employed in order to (i) obtain physical understanding about the roles of specific reactions in the ignition process, and (ii) identify the variables that govern the dynamics of ignition. The following CSP tools were employed: (i) the time scale participation index (TPI), which measures the contribution of each reaction to the time scale of each CSP mode [34], and (ii) the CSP Pointer, which identifies the variables that mostly relate to each CSP mode [35,36]. The CSP basis vectors were approximated by the right and left eigenvectors of the Jacobian of the chemical source term [33,37]. The time scale introduced by the chemical source term is approximated by $\tau_n = |\lambda_n|^{-1}$, where λ_n the eigenvalue of the n-th CSP mode, $n=1,...,N$, and N is the total number of variables.

This work employs CSP to identify reactions which contribute to characteristic time scales that are explosive in nature. A similar analysis was recently performed for n-hexane/air auto-ignition [20] at conditions exhibiting two-stage heat release characteristics. The present work focuses on utilizing these tools to investigate unique features of the three-stage heat release phenomenon. Thus, adiabatic constant volume auto-ignition of n-heptane/air at 720 K and 40 atm was investigated at fuel lean ($\phi = 0.3$) and stoichiometric ($\phi = 1$) conditions using the chemical kinetic model of Zhang et al. [6].

3. Results and Discussion

3.1. Chemical kinetic modeling

The auto-ignition of n-heptane/air mixtures in a homogenous batch reactor was simulated across a range of initial pressures (20-60 atm), temperatures (500-1200 K), and equivalence ratios (0.3, 0.5, and 1.0). Temperature and HRR profiles were plotted for selected conditions and investigated; a few exemplary cases are presented in the main text, while the remaining are given in the Supplementary Material. Figure 1 presents the first (τ_1), second (τ_2), and total (τ_T) IDTs for n-heptane/air mixtures at 40 atm, 720 K, and two equivalence ratios (0.3 and 1.0) under constant volume conditions. As expected, typical single-stage and/or two-stage heat release is observed for stoichiometric n-heptane/air mixtures across the entire range of pressures explored. Stoichiometric fuel/air mixtures at 40 atm (Figure 1) exhibit notable two-stage heat release in the temperature range of 800-950 K. Both τ_1 and τ_T exhibit NTC behavior, which has been discussed previously by Liang and Law [18].

Heat release and ignition characteristics are notably different at $\phi = 0.3$, wherein three distinct stages of heat release are observed at pressures ranging from 20 to 60 atm. For example, lean mixtures at 40 atm (Figure 1) display three-stage heat release in the temperature range of 625-950 K. The first-stage heat release resulting in τ_1 is up to 7 times shorter than τ_T , while the second-stage heat release resulting in τ_2 is up to 1.3 times shorter than τ_T . The ratios $\tau_1: \tau_T$ and $\tau_2: \tau_T$ depend on pressure, temperature, and equivalence ratio. Simulations with n-heptane kinetics models from Cai et al. [28] and Pelucchi et al. [29] yielded similar qualitative results, indicating that three-stage heat release is not an artifact of the kinetic model employed herein.

Figure 1 – Simulated IDTs of n-heptane/air mixtures at 40 atm, 720 K, and equivalence ratios of (left axis) 0.3 and (right axis) 1.0.

Additional features of three-stage heat release are presented in Figure 2, wherein temperature, HRR, and species mole fraction profiles are presented for the 40 atm, 720 K, $\phi = 0.3$ case. At the end of τ_1 , a first stage of heat release raises the temperature by ~ 210 K, which is then followed by a delay period. At the end of τ_2 , a second stage of heat release raises the temperature by another ~ 370 K; this is followed by another delay period, and finally a slow third-stage heat release regime increases the temperature by an additional ~ 320 K to ~ 1620 K. The HRR profile shows three distinct stages of heat release. Under the conditions of Figure 2, the first-stage HRR is the largest of the three, followed by the second-stage HRR, and finally the small third-stage HRR. This is notably different than the observed two-stage heat release phenomenon at stoichiometric conditions (refer to Figure S1 in Supplementary Material), wherein the first-stage LTHR peak is orders of magnitude smaller than the second-stage HTHR peak. Simulations under isobaric (constant pressure) conditions also showed three-stage heat release at lean conditions (refer to Figure S2)

Species profiles (Figure 2) for the representative three-stage heat release case also show unique features. Hydroxyl (OH) and HO_2 radicals are important drivers of ignition processes; these radicals reach local maxima at the end of τ_1 and τ_2 , respectively, which indicates their importance towards these stages of heat release. The concentrations of these radicals decrease immediately after τ_1 and

after τ_2 . During the third-stage heat release, OH radical concentration increases monotonically, while HO₂ radical profiles plateau and then decrease. The CO concentration increases at the end of τ_1 , and then continues to rise to a maximum at the end of τ_2 . During the third-stage heat release regime, CO concentrations decrease slowly, as it is converted to CO₂. The slow decay of CO and HO₂ concentrations during the third-stage heat release suggests the presence of some inhibitory reactions, which are later elucidated using CSP analysis.

Figure 2 – Simulated (left) temperature and HRR and (right) species mole fractions for n-heptane/air mixtures at 40 atm, 720 K, and $\phi = 0.3$. Shaded regions denote the first (τ_1), second (τ_2), and total (τ_T) IDTs.

3.2. RCM experiments

RCM experiments were conducted to further corroborate the existence of three-stage heat release in the auto-ignition of lean n-heptane/air mixtures. The experiments were conducted at EOC conditions where three-stage heat release was predicted by simulations (i.e., $\phi=0.3$ and 21 atm). Figure 3 presents experimental pressure and CO measurements at 780 K. It should be noted that reactions and heat release were not observed during the compression stroke. An initial increase in pressure is observed shortly after EOC, which corresponds to τ_1 . This is followed by a delay period and subsequently a second-stage heat release resulting in τ_2 . Finally, a third-stage heat release elevates the system to its

final pressure and fully burned condition. The CO profile shows similar behavior as predicted numerically in the three-stage heat release case. The CO concentration profile increases at the end of τ_1 , and then gradually rises to its maximum at the end of τ_2 , and slowly decays during the third-stage heat release regime. Overall, the three-stage heat release behavior predicted by kinetic modeling is in excellent agreement with experimentally observed features at 780 K. Three stage ignition was also observed at temperatures from 808 to 872 K, as shown in the Supplementary Material Figure S3. Three stage ignition was not observed in RCM experimental measurements below 750 K and above 900 K.

Figure 3 - RCM pressure and CO mole fraction profiles for n-heptane/air mixture ($\phi=0.3$). End of compression (EOC) conditions are 780 K and 21.6 atm.

3.3. CSP analysis

CSP analysis was performed for lean and stoichiometric cases at 720 K and 40 atm to better understand the three-stage heat release process. The time scales that characterize the dynamics of the two cases are displayed in Supplementary Material Figure S4, and discussed therein. Our previous work [20,34] showed that the fastest explosive time scale (τ_e) is the characteristic time scale in auto-ignition dynamics. Therefore, the reactions generating τ_e are investigated in the following.

The evolutions of the explosive time scales and temperature are displayed in Figure 4 and Supplementary Figure S5 for the fuel lean ($\phi=0.3$) and stoichiometric ($\phi=1.0$) cases, respectively. The temperature profiles exhibit three-stage heat release in the fuel lean case (Figure 4) and two-stage heat release in the stoichiometric case (Figure S5). In both cases, four key observations are noted: (i) each

ignition stage is characterized by a distinct set of explosive timescales, (ii) τ_e remains roughly constant till the end of the first ignition stage, (iii) at the end of the first ignition stage τ_e disappears and reappears shortly afterwards, and (iv) the points where τ_e disappears lies just before temperature is about to reach a local/global maximum rate of change. In addition, in the fuel lean case, the value of τ_e during the third-stage of heat release is significantly higher than its value during both first and second stages, suggesting that the reactivity of the system decreases compared to the previous stages. It is also noted that during the most part of first stage, τ_e has roughly the same value in both lean and stoichiometric mixtures. However, at the end of the first stage, τ_e decreases more in the stoichiometric case, reaching a minimum of 8.1×10^{-6} sec, as opposed to the fuel lean case which reaches a minimum of 9.1×10^{-5} sec. Based on the profiles of τ_e , representative time instants during the ignition evolution, denoted by P_1 to P_6 (lean case) and P_1 to P_5 (stoichiometric case) were selected and investigated using CSP tools, as shown in Figure 4 and Figure S5, respectively.

Figure 4 - The developing explosive time scales (red-solid lines) overlaid with the temperature profile (blue-dashed line) for lean ($\phi=0.3$) n-heptane/air mixtures at 720 K and 40 atm. The right figure is a zoomed-in view of the left.

Table 1 summarizes all reactions and reaction groups (denoted by “RG”) that were identified as important contributors to the generation of τ_e in both cases under investigation. In the following, the subscripts “f” and “b” stand for forward and backward, respectively, reaction or reaction group. The following discussion focuses on the lean case displaying three-stage heat release. Commentary on the stoichiometric case displaying two-stage heat release is similar to that previously presented for n-hexane [20] auto-ignition.

Table 1: The reactions (XX) and reaction groups (RGXX) providing significant contribution to the generation of the fast explosive timescale for lean ($\phi=0.3$) n-heptane/air mixtures at 720 K and 40 atm; R in RO₂: C₇H₁₅, Q in QOOH and O₂QOOH: C₇H₁₄, Q' in OQ'=O: C₇H₁₃, KHP: keto-hydroperoxides.

1: H+O ₂ ↔ O + OH	15: HO ₂ + HO ₂ ↔ H ₂ O ₂ + O ₂	RG1: C ₂ H ₄ + OH ↔ products
2: H ₂ + OH ↔ H + H ₂ O	17: H ₂ O ₂ (+M) ↔ 2OH (+M)	RG4: RO ₂ ↔ QOOH
4: O + H ₂ O ↔ 2OH	21: H ₂ O ₂ + OH ↔ H ₂ O + HO ₂	RG5: RO ₂ ↔ olefins + HO ₂
9: H + O ₂ (+M) ↔ HO ₂ (+M)	25: CO + OH ↔ CO ₂ + H	RG6: QOOH + O ₂ ↔ O ₂ QOOH
11: H + HO ₂ ↔ H ₂ + O ₂	148: CH ₃ + O ₂ (+M) ↔ CH ₃ O ₂ (+M)	RG7: O ₂ QOOH ↔ KHP + OH
13: OH + HO ₂ ↔ H ₂ O + O ₂	331: C ₂ H ₃ + O ₂ ↔ CH ₂ CHO + O	RG16: KHP ↔ OQ'=O + OH

Table 2 includes the CSP diagnostics (TPI of τ_e and CSP pointer Po of the related explosive mode) for both the lean (shaded columns) and stoichiometric (italic font) simulations. Points P₁-P₂ represent the first-stage heat release, while P₃-P₄ and P₃-P₅ represent the second-stage heat release under lean and stoichiometric conditions, respectively. P₅-P₆ represents the third-stage heat release under lean conditions. Chemical characteristics for each stage of the ignition process are examined in the following discussion.

Reactions highlighted as important during the first stage (P₁-P₂) are those typically characterizing low-temperature oxidation of alkanes. In particular, the route of RG4_f→RG6_f→RG7_f→RG16_f leads eventually to the formation of two OH molecules, therefore all involved reaction groups favor the explosive character of τ_e and promote ignition. On the other hand, both RG4_b and RG5_f compete with RG4_f (and as a result of the aforementioned path); these oppose the explosive character of τ_e and retard ignition. Initially, the CSP pointer Po identifies KHP, RO₂ and O₂QOOH as the variables that are mostly related to the fast explosive mode; KHP is a reactant in group RG16_f, i.e., the largest contributor to τ_e , RO₂ is reactant in RG4_f and RG5_f, both of which are significant contributors to τ_e , and O₂QOOH is reactant in RG7_f. At the end of the first-stage heat release, however, temperature becomes the most important pointer to the explosive mode, indicating a transition from chemical to thermal runaway. The reactions and species contributing to the first stage of heat release in the fuel lean case are similar to those in the stoichiometric case, although the temperature reaches 861 K in the stoichiometric case and 766 K in the lean case at the end. These results suggest that the first-stage heat release is

characterized by the same chemical pathways in the fuel lean and stoichiometric cases; however, the stoichiometric mixture enters the thermal runaway sooner due to the increased temperature.

Table 2: Values of the largest TPI and CSP pointer Po of the fast explosive mode for lean ($\phi=0.3$, shaded column) and stoichiometric ($\phi=1.0$, italic font) n-heptane/air mixtures at 720 K and 40 atm. Refer to Fig. 2 and Fig. S3 for the selected points P₁-P₆.

	P ₁		P ₂		P ₃		P ₄		P ₅		P ₆									
t [s]	0.00E+00	0.00E+00	2.20E-03	1.98E-03	2.93E-03	2.05E-03	3.22E-03	2.07E-03	3.46E-03	2.07E-03	3.96E-03									
τ _c [s]	1.26E-04	1.17E-04	9.60E-05	3.95E-05	3.24E-04	9.10E-06	6.94E-05	1.36E-06	1.27E-03	2.29E-07	5.96E-04									
T [K]	720	720	736	755	972	1141	1108	1588	1340	1990	1465									
TPI	RG16 _f	15.9%	15.9%	RG4 _f	21.7%	12.7%	17 _f	20.4%	17 _f	20.4%	17 _f	24.1%	1 _f	28.5%	13 _f	-18.9%	1 _f	37.6%	1 _f	25.2%
	RG4 _f	10.8%	10.4%	RG16 _f	12.4%	12.4%	21 _f	-7.1%	RG1 _f	5.9%	13 _f	-8.6%	13 _f	-5.6%	1 _f	17.9%	9 _f	-7.6%	13 _f	-23.8%
	RG4 _b	-9.1%	-9.1%	RG4 _b	-10.6%	-10.6%	15 _f	-6.0%	13 _f	-5.3%	RG1 _f	6.6%	RG1 _f	4.9%	25 _f	13.0%	2 _f	5.8%	9 _f	-14.3%
	RG6 _f	9.0%	9.0%	RG6 _f	8.3%	8.3%	RG1 _f	3.0%	11 _f	-3.6%	21 _f	-6.3%	11 _f	-4.3%	9 _f	-7.2%	13 _f	-5.8%	25 _f	13.0%
	RG7 _f	8.6%	9.0%	RG5 _f	-5.2%	-5.2%					25 _f	3.4%					25 _f	5.1%	4 _f	7.2%
	RG5 _f	-5.2%	-5.4%	RG7 _f	3.9%	4.5%													9 _b	5.8%
CSP Po	KHP	0.46	0.5	T	0.55	0.65	T	1.15	T		T	1.76	T	1.31	T	2.47	T	1.11	T	2.24
	RO ₂	0.17	0.16	KHP	0.38	0.15	H ₂ O ₂	-0.07	H ₂ O ₂	-0.24	H ₂ O ₂	-0.44	C ₂ H ₄	-0.1	CO	-0.85	O ₂	-0.15	CO	-1.11
	O ₂ QOOH	0.1	0.1	RO ₂	0.13	0.12														

The second stage, represented by P₃-P₄ (lean) and P₃-P₅ (stoichiometric) is investigated next. As shown in Figure 4, τ_e gradually increases and then decreases during this period under lean conditions, while it decreases continuously under stoichiometric conditions. Hydrogen-related oxidation chemistry plays an important role in the second stage, as indicated by the TPIs at points P₃-P₄ in Table 2. In particular, the gradual acceleration of τ_e is associated with the increased role of 17_f, which dissociates H₂O₂ to two highly reactive OH radicals, thereby promoting auto-ignition. This reaction is important under both lean and stoichiometric conditions, while 1_f (H+O₂↔O+OH) plays a significant role at P₄-P₅ represent under stoichiometric conditions. The major opposition to the generation of τ_e under lean conditions is by reaction 21_f, which competes with 17_f by consuming H₂O₂, but this reaction does not play a significant role under stoichiometric conditions. Under lean conditions, additional opposition to the explosive character is provided initially by 15_f (HO₂+HO₂↔H₂O₂+O₂) and subsequently by 13_f (OH+HO₂↔H₂O+O₂) which are both radical terminating reactions. 13_f is also important under stoichiometric conditions, in addition to other termination reactions 11_f (H+HO₂↔H₂+O₂) and 9_f (H+HO₂+M↔HO₂+M). The role of RG1_f (which is the only carbon-related reaction with significant

contribution to τ_e) is also highlighted under both conditions, favoring the explosive character of τ_e . The role of this reaction has also been reported during the second ignition stage of n-hexane [20].

Based on the results displayed in Table 2, the second-stage heat release under stoichiometric conditions begins with H_2O_2 decomposition and quickly transitions to $\text{H}+\text{O}_2$ chain branching resulting in thermal runaway. Under lean conditions, the second-stage heat release is affected by the competition between hydrogen- and carbon-related chemistry as follows: the OH radicals produced by 17_f can either undergo the route of $21_f \rightarrow 15_f$ or react with C_2H_4 through $\text{RG}1_f$. Gradually, the role of chain terminating reactions becomes more important under lean conditions as they are enhanced by the contribution of reaction 13_f . Therefore, eventually τ_e starts decreasing under lean conditions. The CSP Po identifies temperature as the variable mostly related to the fast explosive mode, thus, verifying that the second stage is in the thermal runaway regime. Additionally, the importance of H_2O_2 is also highlighted by the CSP Po, since it is the reactant of 17_f , i.e., the largest contributor to τ_e , while C_2H_4 and O_2 are also key species under stoichiometric conditions.

Finally, the third heat release stage ($\text{P}_5\text{-P}_6$) under lean conditions is dominated exclusively by hydrogen-related and CO-to- CO_2 chemistry, as shown in Table 2. In particular, the contribution of 13_f , which was found to be significant at the last part of the second stage, becomes dominant at the initial part of the third stage and remains significant throughout. Unlike the second stage, reaction 13_f now competes with 25_f ($\text{CO}+\text{OH} \leftrightarrow \text{CO}_2+\text{H}$) and 9_b , which both provide considerable contribution to the generation of τ_e , favoring its explosive character. The highly exothermic reaction 25_f is the major CO-to- CO_2 reaction path and the endothermic reaction 9_b dissociates HO_2 to produce H radicals. This inhibition of CO oxidation explains the slow decay of CO observed previously in simulations (Figure 2) and experiments (Figure 3). Our explanation for slow CO to CO_2 conversion is consistent with that of Sjöberg and Dec [38] in lean burn engines. The major positive contributor to τ_e is the chain branching reaction 1_f ($\text{H}+\text{O}_2 \leftrightarrow \text{O}+\text{OH}$) which becomes significant at this stage, provided that the temperature has increased sufficiently. However, the chain termination reaction 9_f is active and

competes with 1_f . The CSP Po identifies temperature as the variable mostly related to the fast explosive mode, which is reasonable considering that the third stage relates to the thermal runaway regime. Additionally, the CSP Po identifies CO which is a reactant in 25_f . In conclusion, the increased value of τ_e and slow reactivity during the third stage is mainly attributed to the increased influence of reactions 13_f and 9_f , which both oppose the explosive character of τ_e . The former competes with 25_f and 9_b , absorbing OH radicals produced by (mainly) 1_f and 4_f , while the latter competes directly with the main chain branching reaction 1_f . The reaction 9_f ($\text{OH} + \text{HO}_2 \leftrightarrow \text{H}_2\text{O} + \text{O}_2$) has been an experimental target for kinetic measurements [39], since this reaction plays important role in high pressure lean combustion of methane [40]. However, this reaction has received little attention in liquid fuel (e.g., *n*-heptane) combustion, and is shown here to be important in three-stage ignition under lean conditions.

4. Conclusions

This study presents initial findings of three-stage heat release in the auto-ignition of *n*-heptane/air mixtures at lean conditions, high pressures, and low-to-intermediate temperatures. The presence of three-stage heat release was initially found by performing detailed kinetic modeling simulations in a homogenous batch reactor. IDT profiles under lean conditions showed three distinct stages of ignition, i.e., first-stage ignition, second-stage ignition, and final ignition, which was remarkably different than behavior observed at stoichiometric conditions. Pressure and CO profiles measured in an RCM confirmed the existence of three-stage heat release under specific conditions of temperature, pressure, and equivalence ratio.

CSP analysis revealed that first-stage heat release in lean and stoichiometric conditions is governed by the same set of reactions and species/thermal indicators. However, the second-stage heat release leads to thermal runaway in the case of stoichiometric mixtures, but not in lean mixtures. Instead, CO oxidation and $\text{H} + \text{O}_2$ chain branching reactions are inhibited by radical terminating reactions that consume OH and HO_2 radicals. The reaction $\text{H} + \text{O}_2 (+\text{M}) = \text{HO}_2 (+\text{M})$ has long been identified as important for governing the ignition limits of hydrogen/air mixtures; however, the role of

$\text{OH} + \text{HO}_2 \leftrightarrow \text{H}_2\text{O} + \text{O}_2$ has thus far received little attention in liquid fuel combustion. The present work demonstrates that hydrocarbon ignition under high pressure and lean conditions reveals a new heat release regime and chemical kinetic phenomenon that warrant further investigation.

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