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Modeling Pre-Spark Heat Release and Low Temperature Chemistry of Iso-Octane in a Boosted Spark-Ignition Engine

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Abstract: Recent trends among automotive manufacturers towards downsized, boosted engines make it imperative to understand specific fuel chemistry interactions encountered in this new operating regime. At these elevated pressure conditions a phenomenon called pre-spark heat release (PSHR) has recently been discovered, characterized by kinetically controlled heat release before spark, leading to changes in end-gas thermodynamic state and composition. These reactions typically occur in the end-gas during normal operation, but are obscured by the deflagration heat release, and therefore cannot be easily studied. A 2-zone spark-ignition engine model was utilized to determine whether chemical kinetic mechanisms predict this phenomenon, and whether they accurately capture end-gas thermodynamic history. Experimental engine data at a range of boosted operating conditions demonstrating PSHR were compared with simulations using mechanisms representing the latest developments in gasoline kinetic modeling. The results demonstrated significant discrepancies between mechanisms, and between experimental and simulated results in terms of low-temperature heat release magnitude and end-gas thermodynamic state. That none of the un-tuned mechanisms matched the experimental results highlights shortcomings in low-temperature reaction pathways, and indicate the necessity of simultaneously matching first-stage ignition delay and heat release magnitude, in addition to second-stage ignition delay, in order to accurately predict end-gas thermodynamics and knock.
Keywords: Low Temperature Chemistry, Chemical Kinetics, Knock, SI Engines

1. Introduction

Concerns over global carbon dioxide (CO2) emissions and pressure from regulatory agencies have driven engine manufacturers in recent decades towards engine technological advancements such as gasoline direct injection, variable valve timing, engine downsizing, and turbocharging. These technologies have resulted in significant improvements in vehicle fuel economy to date, while further efficiency gains are possible with improved knock resistance from the fuel [1]. The high in-cylinder pressures, and high specific load requirements in these modern engines have brought about challenges associated with pre-ignition phenomena including low-speed pre-ignition (LSPI) [2]. In the US, gasoline fuels are sold based on the Anti-Knock Index (AKI), which represents the average of the Research Octane Number (RON) [3] and Motor Octane Number (MON) [4] of the fuel. These two test conditions represent different pressure-temperature trajectories due to variations in the inlet mixture temperature; MON representing a higher temperature condition [5]. The difference between RON and MON is referred to as the Octane Sensitivity, and is a relative measure of the sensitivity of a fuel to operating conditions compared

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to the primary reference fuels used to define the RON and MON scales [3,4]. Many researchers have shown the benefits of both high octane and high sensitivity fuels on engine performance and thermal efficiency in boosted engines [5,6], and Splitter et al. [1] discusses potential efficiency improvements through the adoption of higher ethanol (which has high octane sensitivity) blending fractions to increase octane number, allowing for the use of higher compression ratios.

Szybist and Splitter [5] identified a new phenomenon called pre-spark heat release (PSHR) for iso-octane and gasoline fuels at elevated intake pressure and temperature conditions, and found that the tendency towards PSHR decreased with increasing octane sensitivity. They demonstrated that PSHR is a kinetically-controlled phenomenon, and not caused by an independent deflagration event. In a subsequent work, Splitter et al. [2] showed that PSHR magnitude correlated with LSPI frequency, but that the occurrence of PSHR was not necessarily an indicator of LSPI potential. Because PSHR is a distinct process from deflagration, it can be used as a tool to assess kinetic mechanism thermodynamic and knocking predictions at stoichiometric conditions for gasoline-relevant fuels without needing to model the deflagration process in significant detail. A mechanism which adequately predicts end-gas thermodynamic conditions for cases demonstrating PSHR would then provide confidence when simulating cases where low temperature heat release (LTHR) takes place during the main deflagration event where it would otherwise be obscured.

2. Methodology

a. Experimental Approach

Iso-octane was chosen for the preliminary analysis because its chemical kinetics have been extensively studied by numerous researchers including [7,8], due to its relevance in the standard RON [3] and MON [4] test methods, and because it is a fuel which exhibits negative temperature coefficient (NTC) behavior [7]. Iso-octane also comprises a significant portion of many gasoline surrogate fuels [9], representing various iso-alkane components. The experimental data utilized in this work was collected on a 2.0L GM Ecotec LNF engine, the specific geometry and operating conditions studied in this work are shown in Table 1. A more complete description of the laboratory configuration, data collection, and post-processing routines can be found in [5].

Table 1: GM Ecotec 2.0L LNF Engine Geometry and Experimental Operating Conditions

Bore [mm]	86.0	Speed [r/min]	2000
Stroke [mm]	86.0	Airflow [g/min]	804
Conrod Length [mm]	145.5	External EGR [%]	0
Wrist Pin Offset [mm]	0.8	Residual [%]	7-8
IVC [^{o}CA ATDC]	-141	CA50 [^{o}CA ATDC]	32-35
EVO [^{o}CA ATDC]	130	$IMEP_g$ [bar]	14-15
Compression Ratio [-]	9.2[a]:1		

[a]*Reduced to 8.7:1 in post-processing*

A wide range of knocking and non-knocking operating conditions with and without exhaust gas recirculation (EGR) were tested, though this work focuses only on non-knocking cases with a fixed combustion phasing of ~33° after top dead center firing (ATDC), at 6 intake temperatures between 41°C and 131°C with no EGR. The combustion phasing was defined by the CA50 value, which corresponds to the crank angle of 50% mass fraction burned (MFB). These conditions represent stoichiometric, boosted, moderately high load operation with a nominal indicated gross mean effective pressure ($IMEP_g$) of 14-15bar. Figure 1 shows the 2000 cycle ensemble averaged experimental pressure and heat release rate profile for a case which demonstrates fully-developed PSHR, with spark timing denoted on the heat release line. A clear and distinct LTHR event,

reminiscent of that commonly observed in purely kinetically controlled combustion strategies such as Homogeneous Charge Compression Ignition and Partial Fuel Stratification, is present before the spark event, shown in the inset axis. The PSHR at this operating condition ends just after the spark, before any appreciable heat release from deflagration occurs.

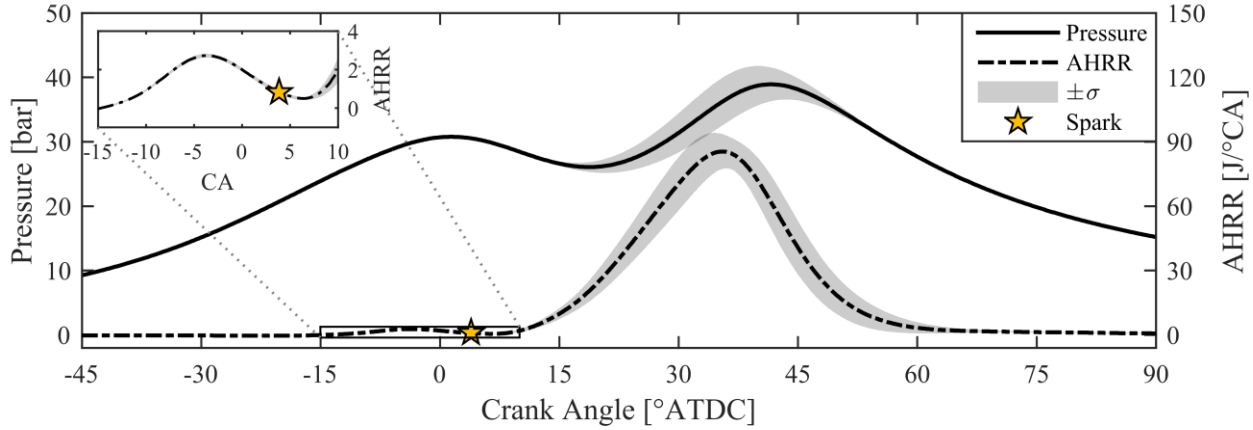

Figure 1: Ensemble averaged pressure and apparent heat release rate vs. crank angle, one standard deviation in shaded grey, at T_{in} = 131°C. Inset axis shows PSHR

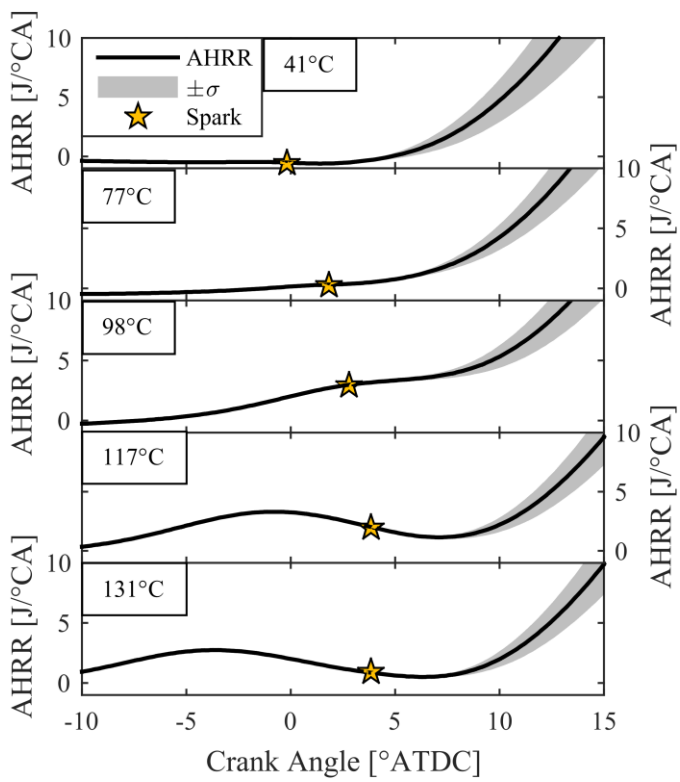

Figure 2: Apparent heat release vs. crank angle in region of potential PSHR for 5 intake temperatures

The evolution of PSHR as a function of intake temperature can be seen in Figure 2, where for the lowest intake temperature investigated (41°C), no discernable PSHR is observed, but for the highest intake temperature (131°C), a clear and distinct PSHR event is observed. Between these extremes (77°C to 117°C), there is evidence of developing PSHR that is not associated with the main deflagration event. At a sufficiently high temperature (117°C), PSHR reaches a local maxima, but at lower temperatures the LTHR blends into the main deflagration. At these elevated

pressure conditions it is very likely that all cases exhibit some amount of LTHR in the end-gas. This process cannot easily be deconvoluted in experimental data for cases where LTHR overlaps the much higher magnitude deflagration heat release, but cases which exhibit LTHR before deflagration allow for this process to be decoupled and modeled with a 2-zone methodology.

b. Modeling Approach

The modeling results shown in this work utilize the built-in zero-dimensional, two-zone Spark Ignited (SI) engine model associated with the Chemkin Pro package in ANSYS® v18.1. This model utilizes detailed chemistry to predict end-gas auto-ignition, i.e. knock, but the solver will predict any chemical heat release, including LTHR, even when knock is not present. The two zones represent the unburned fuel/air/EGR and the burned gases respectively. Mass is transferred between the zones at the rate and timing specified by a user inputted Wiebe function. For each operating condition, the best-fit Wiebe function was determined from the experimental MFB profile with a least-squared error approach by iterating the Wiebe parameters θ_o, $\Delta\theta$, and m, and minimizing the error between the calculated and experimental profile.

The heat transfer correlation utilized in this work was the ubiquitous Woschni formulation [10], with the scaling parameter and cylinder wall temperature tuned to match the experimental pressure. With a fixed scaling parameter, the cylinder wall temperature was made to be a linear function of intake temperature to adequately match the experimental data. Minor tuning to the IVC temperature was required to match the experimental pressure, on the order of 5-15K from the experimentally calculated IVC temperatures, illustrating good overall agreement with the data. The methods used to calculate experimental quantities such as trapped mass, IVC temperature, and residual fraction are discussed in [5]. Residual gas composition was assumed to be identical to the measured exhaust emissions at each operating condition, comprised of only CO_2, water vapor, oxygen, nitrogen, carbon monoxide, hydrogen, nitrogen oxide (NO), and unburned hydrocarbons (uHC). The uHC was assumed to be composed of unburned fuel (i.e. iso-octane).

3. Results and Discussion

The first step in analyzing the effects of PSHR was ensuring that the thermodynamic conditions (i.e. temperature and pressure) of the end-gas can be accurately modeled, given the sensitivity of phenomena like knock and LSPI on the thermodynamic state of the end-gas [2]. Four recent chemical mechanisms [9,11-13] were selected from the literature to determine whether any of the mechanisms could accurately match the experimental PSHR magnitude and phasing. Each of the selected mechanisms were developed to simulate gasoline surrogate fuel mixtures in engine applications. Figure 3 shows the results of the simulations for each kinetic mechanism compared to the ensemble-averaged pressure and heat release rate at three intake temperature conditions. Spark timing varied in each case to achieve the desired combustion phasing. The representative conditions shown were chosen to demonstrate cases with no PSHR (41ºC), PSHR that blends into the deflagration (98ºC), and fully decoupled PSHR (131ºC).

Each mechanism predicts significant differences in the LTHR magnitude and phasing. The Mehl et al. [9] mechanism predicts no LTHR for any of the cases shown, while Cai et al. [12] and Ren et al. [13] predict similar LTHR phasing to the experiments at 98ºC and 131ºC, and Andrae et al. [11] predicts a delayed LTHR event, and even predicts high-temperature auto-ignition (i.e. knock) in the 131ºC case despite no evidence of knock in the experimental data (experimental knock limit at 131ºC was 9ºCA more advanced than present analysis). For the mechanisms that show PSHR, there is a small peak due to low-temperature reactions in the unconsumed end-gas near the peak heat release rate for the 41ºC case, though this LTHR is indiscernible from the deflagration heat release in the experimental data. Based on emissions measurements and residual

fractions, the highest residual NO levels were about 100ppm at IVC. Given the important role of NO_x in the fuel oxidation and radical formation processes even in low concentrations [14], it is not surprising that the two mechanisms that include NO_x chemistry (i.e. Ren et al. and Cai et al.) provide the best predictions of LTHR phasing and magnitude, while the mechanisms that do not (i.e. Mehl et al. and Andrae et al.) do not agree well. This result reinforces the importance of the inclusion of NO_x chemistry in chemical kinetic mechanisms for knock prediction.

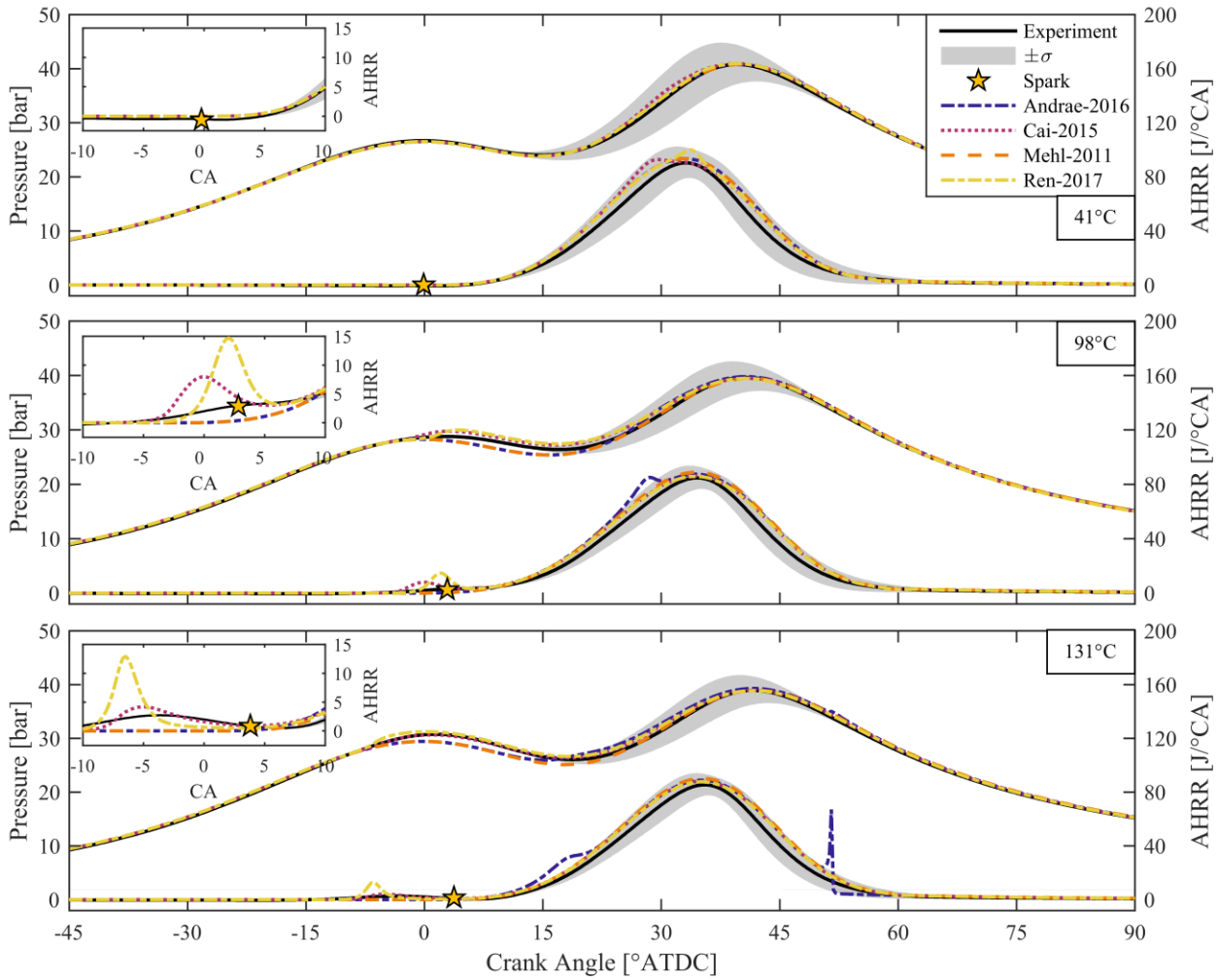

Figure 3: Pressure and apparent heat release vs. crank angle, comparing experimental data (black) including standard deviation (grey) at three intake temps (41°C, 98°C, and 131°C), and simulations for 4 mechanisms

In order to better understand the discrepancies observed in Figure 3, ignition delay simulations were performed for the four tested kinetic mechanisms via two methods. The first utilized rapid compression machine (RCM) simulations performed in Chemkin Pro using a closed homogeneous batch reactor model to simulate RCM experiments for iso-octane collected from literature [15]. This dataset in particular was chosen because the authors provided both calculated RCM volume traces, and measured pressure data, allowing for a more rigorous comparison than ignition delay alone. The variable volume profile was specified in the reactor model, and the initial temperature and pressures were set to achieve the appropriate end-of-compression (EOC) state. Three EOC temperatures were simulated (704K, 814K, and 852K), all at an EOC pressure of 20 bar. In a recent work, Salih et al. [16] showed that the same 814K, 20 bar case's thermodynamic trajectory matches well with the trajectory for iso-octane under RON operating conditions until the EOC state, while

the 704K, 20 bar case would represent a "beyond RON" condition, more representative of the engine operating conditions in this work.

The second set of ignition delay simulations utilized a constant volume (CV), homogeneous, adiabatic reactor model solved using the Cantera toolbox in Matlab® at an initial pressure of 20 bar, and a wide range of initial temperatures. Ignition (corresponding to "2nd Stage Ignition") was defined as the time of maximum rate of temperature change, while "1st Stage Ignition" was defined if a local maxima in the rate of temperature change was detected before the main ignition event. Additionally, if a distinct 1st stage ignition event was detected, the magnitude of this event (in K) was defined as the difference in temperature between the point of local minima in rate of temperature change between 1st and 2nd stage ignition, and the initial temperature. All experimental and simulated ignition delay cases presented here were at stoichiometric conditions with no residual gas or EGR considered.

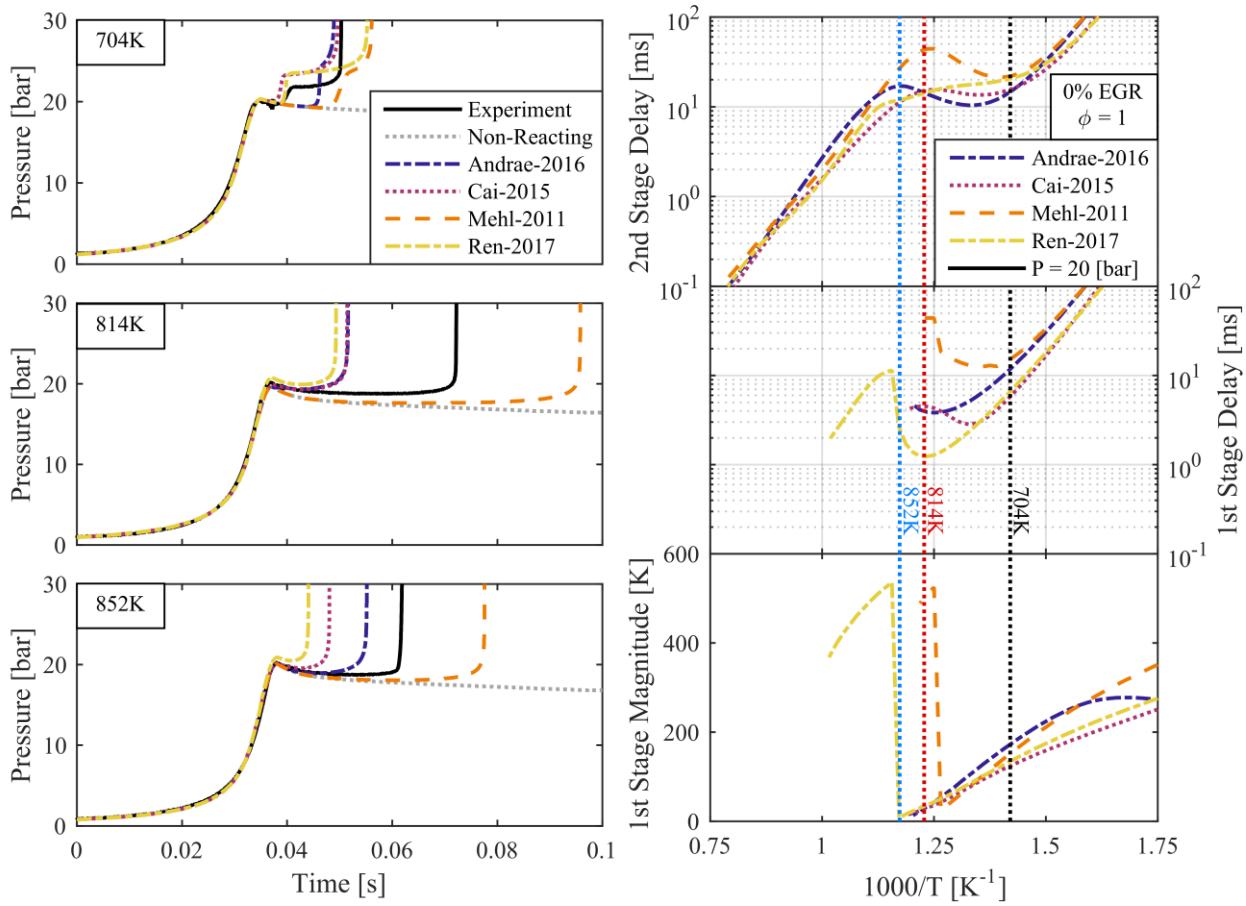

Figure 4: RCM simulations compared to experiments at 704K, 814K and 852K and EOC pressure of 20 bar for the four tested mechanisms (left), and constant volume ignition delay simulations highlighting second stage (high-temperature) ignition delay, and first stage (low-temperature) ignition delay and magnitude (right)

Figure 4 shows the results of the RCM simulations (left) and CV simulations (right) at the conditions described. For reference, the three RCM simulation EOC temperatures are highlighted on the CV ignition delay simulation plots. It can clearly be seen from both figures that significant differences can be observed between mechanisms for even a well-studied fuel like iso-octane, including large differences in 1st and 2nd stage ignition timing, as well as 1st stage magnitude. From the RCM simulations, a similar trend to the engine simulations shown in Figure 3 can be observed for the 704K case with respect to the LTHR magnitude and phasing (i.e. that the Ren et al. and Cai

et al. mechanisms match LTHR phasing, but over-predict the magnitude). These results highlight some obvious and significant discrepancies that exist in the mechanisms available in the literature.

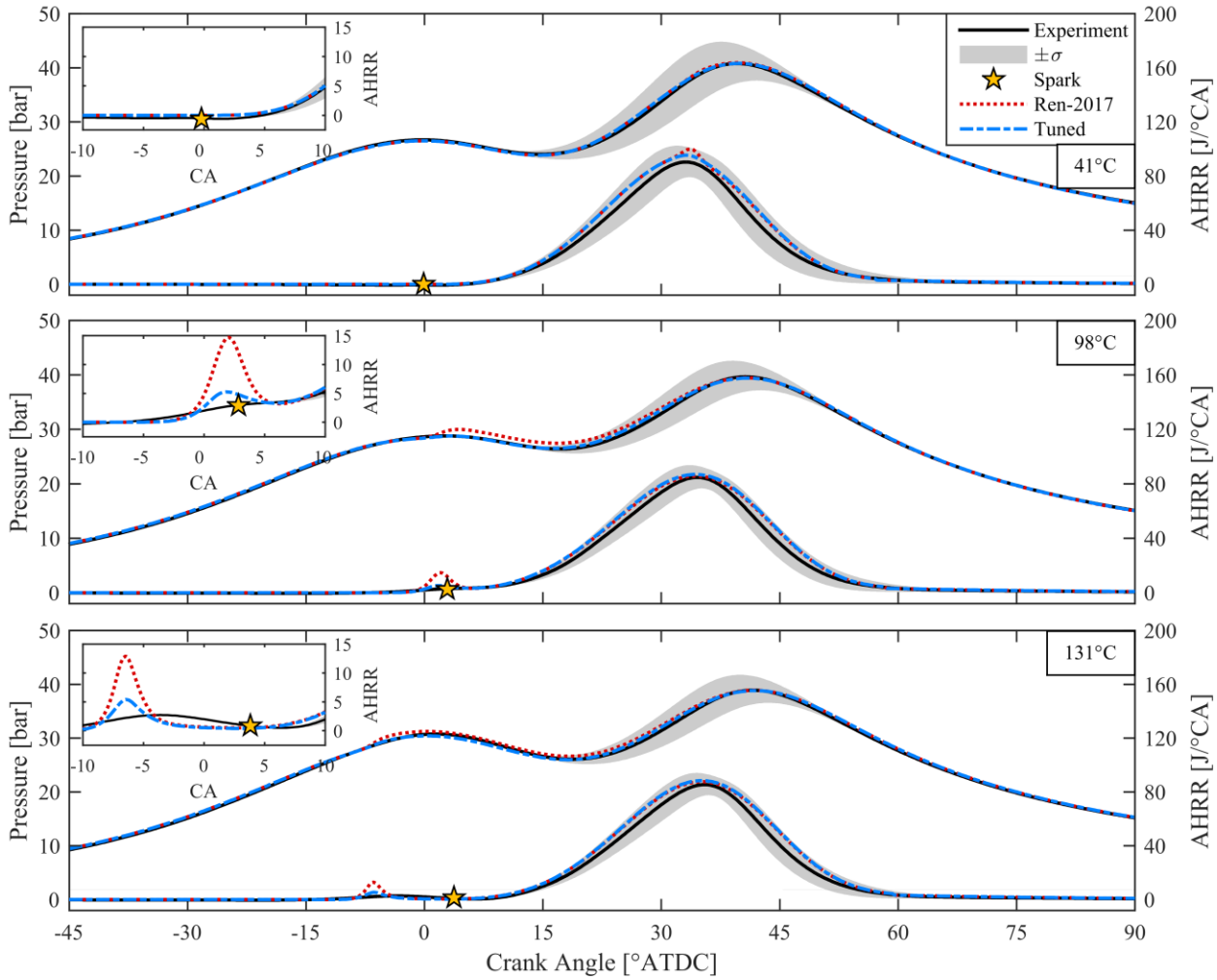

Figure 5: Pressure and apparent heat release vs. crank angle comparing experimental data (black lines) including standard deviation (grey) at three intake temperatures (41ºC, 98ºC, and 131ºC), comparing the original Ren et al. [13] (red dotted) mechanism and the tuned version (blue dash dotted)

It is reasonable to assume that if a kinetic mechanism could accurately predict the LTHR phasing and magnitude for cases which exhibit PSHR at a wide range of temperature-pressure histories and mixture compositions, then the same mechanism should predict LTHR in the end-gas for cases where it is obfuscated by the main deflagration, as would be the case in typical knocking conditions. The Ren et al. mechanism was chosen for further study to determine whether specific reactions could be tuned to better match the experimental results. It was chosen over the Cai et al. mechanism since it tended to accurately predict the phasing of the PSHR event for all the tested cases, but with a systematically elevated magnitude, while Cai et al. demonstrated non-linearity in the agreement between the simulations and experiments, and therefore would likely require a more involved tuning procedure.

The approach utilized was to first identify the important pathways in the low-temperature oxidation process. These have been well defined in literature, including Zhao et al. [17], who outlined the dominant chemical reactions and pathways in the first-stage ignition of n-heptane which, while not studied in the current work, follows the same general processes as iso-octane.

Given the general trend in the simulations (i.e. accurate LTHR timing, but elevated magnitude), it was necessary to decrease the amount of fuel that decomposed via low-temperature reactions. The approach that worked most universally was to decrease the rate of hydrogen abstraction by OH radicals (i.e. $iC_8H_{18} + OH \rightarrow aC_8H_{17} + H_2O$) by decreasing the pre-exponential factor from 7.5×10^6 to 2.5×10^6. This change tended to decrease the magnitude without changing the timing of the LTHR event. It should be noted that this change has a significant effect on the 2nd Stage ignition delay prediction under conditions where LTHR is relevant, particularly for "beyond RON conditions" as discussed in Salih et al. [16], which utilized this same tuning. This tuned mechanism thus provides *worse* knock prediction capability under the conditions studied here, but the focus of this work is on the end-gas thermodynamics, and not knock prediction. Figure 5 shows comparisons between the experimental traces and the original and tuned Ren et al. predictions. The tuned mechanism provides significantly better agreement, demonstrating the validity of the tuning approach. While the phasing agrees well, the duration of the LTHR events are not well captured despite very similar pressure traces. This discrepancy is primarily a result of the single, lumped unburned zone in the Chemkin 2-zone model. Despite this, it is reasonable to assume that the mean unburned thermodynamic conditions are matched well given the excellent agreement between the experimental and tuned mechanism pressure traces.

Constant volume ignition delay simulations were again performed in Matlab® using Cantera over a wide range of conditions using the tuned Ren et al. mechanism to develop the ignition delay contours shown in Figure 6. Ignition here was defined as a 50K temperature rise from the initial state. This provides a consistent metric representing a significant energy release via chemical reactions in the mixture (which could correspond to first-stage or second-stage ignition depending on thermodynamic conditions). The predicted temperature/pressure trajectories of the end-gas were overlaid on the ignition delay contours for three different intake temperatures, with the controlling mechanism of temperature/pressure change denoted, and were truncated at the crank angle of 98% MFB. Portions of the paths where dotted and dashed lines overlap (e.g. for the 41ºC case) indicate LTHR occurring during the main deflagration event.

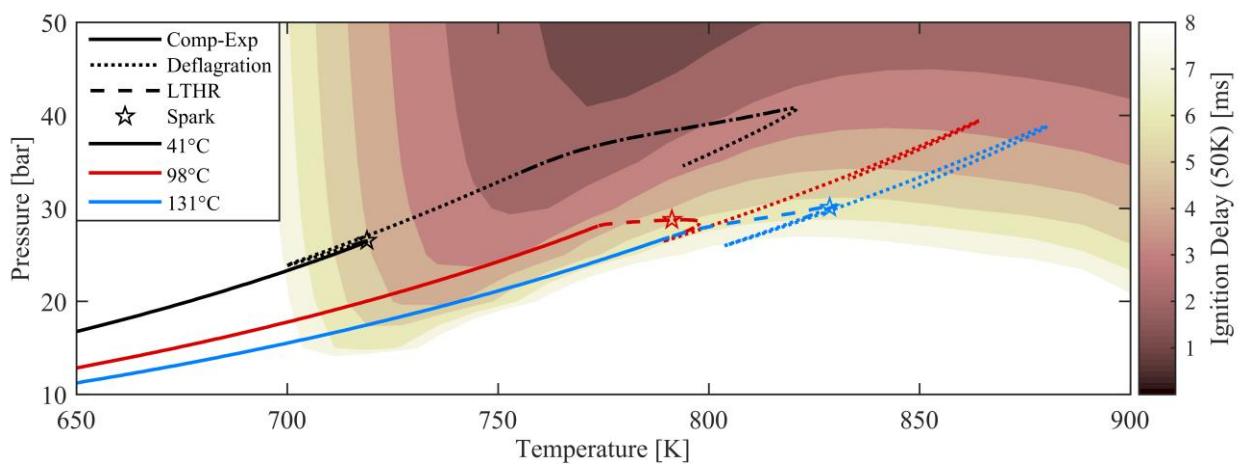

Figure 6: Predicted unburned P-T trajectories for three intake temperatures overlayed on ignition delay contours (ignition defined as 50K temperature rise). Linestyle represents mode of temperature/pressure change (Solid: compression and expansion, dotted: compression due to deflagration, dashed: LTHR)

As can be seen in the figure, the LTHR acts as a nearly iso-baric temperature increase in the end-gas, while the compression/expansion and deflagration processes act via polytropic compression/expansion. The inflection depends on whether the pressure was increasing or decreasing when the LTHR event occurred, and whether the LTHR magnitude offsets the pressure

change due to expansion. For the 41°C case, the LTHR event occurs near the location of maximum heat release rate where the cylinder pressure is increasing due to deflagration, while for the 98°C case, the LTHR occurs after TDC during expansion, and in the 131°C case, LTHR occurs before TDC during compression. As is clearly shown, the phasing and magnitude of the LTHR event strongly influences the temperature-pressure history of the end-gas.

For iso-octane, which demonstrates strong NTC behavior at these conditions, the temperature increase actually results in an increase in the first-stage ignition delay, thus it seems as if this process is self-regulating for fuels with NTC, i.e. that as the end-gas releases heat via low-temperature reactions, thus increasing temperature, the ignition delay increases to a point where the low-temperature reactions will not occur before the deflagration event consumes the remaining end-gas. Szybist and Splitter [5] noted that for fuels with NTC, once LTHR developed, combustion phasing did not need to be retarded to mitigate knock. For fuels with positive temperature coefficient (PTC) behavior, LTHR could accelerate end-gas chemistry, making these fuels more knock prone, and more susceptible to cycle-to-cycle variations in end-gas composition and state.

High octane sensitivity fuels (which tend to have no NTC, or strong PTC [9]) are less knock prone and more suitable for high boost conditions [5,6], but it is unclear whether LTHR is a positive, negative, or neutral property in terms of a fuel's ability to resist auto-ignition. Szybist and Splitter [5] demonstrated that at high load, high temperature conditions, LTHR-prone fuels operated at higher loads than would be expected based on their RON and MON values, but that a high sensitivity fuel was preferable because it allowed more advanced combustion phasing before reaching the knock limit. Many questions remain, such as whether a fuel that derives a significant amount of its octane sensitivity from heat of vaporization, instead of low-temperature chemistry suppression, may perform worse than a fuel with equivalent or even lower sensitivity at these conditions. As such, the effects of LTHR may help explain discrepancies between predicted and observed octane index values such as those in [5].

4. Conclusions

Experimental conditions exhibiting PSHR were modeled with a 2-zone SI engine model in Chemkin Pro to determine whether literature kinetic mechanisms could accurately capture this phenomena, and thereby end-gas thermodynamic conditions. Four chemical mechanisms representing the state of the art in gasoline surrogate modeling were chosen, and none were able to adequately match experimental results in terms of LTHR magnitude and phasing universally without modification. The two tested mechanisms which incorporated NO_x chemistry were the best performing in terms of LTHR magnitude and phasing, highlighting the importance of NO_x chemistry in SI engine modeling. By tuning a single reaction rate controlling the rate of hydrogen abstraction by OH, the most recent mechanism was able to match the experimental pressure traces with excellent agreement for a range of operating conditions.

The results indicate that it is insufficient for robust chemical mechanisms to match only high temperature ignition delay for knock prediction in boosted SI engines, as a mechanism must match the low temperature ignition delay and heat release magnitude in order to accurately predict the thermodynamic conditions of the end-gas. This methodology provides a pathway towards more robust chemical kinetic mechanism development, since a wide range of conditions exhibit distinct and decoupled PSHR which can be accurately modeled with a simple 2-zone approach as demonstrated in this work, providing a procedure which is more directly relevant to SI engine knock prediction, and more flexible in terms of possible operating conditions than constant volume ignition delay simulations, or rapid compression machine and shock tube experiments.

5. Acknowledgements

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