Impact of Thermodynamic Properties and Heat Loss on Ignition of Transportation Fuels in Rapid Compression Machines

Ahfaz Ahmed^{1*}, Mireille Hantouche², Muneeb Khurshid¹, Samah Y. Mohamed¹, Ehson F. Nasir¹,
Aamir Farooq¹, William L. Roberts¹, Omar Knio³, S. Mani. Sarathy^{1*}

¹Clean Combustion Research Center, King Abdullah University of Science and Technology,
Thuwal, Kingdom of Saudi Arabia

²Mechanical Engineering Department, Physical Science and Engineering Division, King Abdullah
University of Science and Technology, Thuwal, Kingdom of Saudi Arabia

³Computer, Electrical, and Mathematical Science and Engineering, King Abdullah University of
Science and Technology, Thuwal, Kingdom of Saudi Arabia

*Corresponding Author: ahfaz.ahmed@kaust.edu.sa
Clean Combustion Research Center
King Abdullah University of Science and Technology (KAUST)
Thuwal, Kingdom of Saudi Arabia, 23955-6900

*Corresponding Author: mani.sarathy@kaust.edu.sa
Clean Combustion Research Center
King Abdullah University of Science and Technology (KAUST)
Thuwal, Kingdom of Saudi Arabia, 23955-6900

Abstract

Rapid compression machines (RCM) are extensively used to study autoignition of a wide variety of fuels at engine relevant conditions. Fuels ranging from pure species to full boiling range gasoline and diesel can be studied in an RCM to develop a better understanding of autoignition kinetics in low to intermediate temperature ranges. In an RCM, autoignition is achieved by compressing a fuel/oxidizer mixture to higher pressure and temperature, thereby initiating chemical reactions promoting ignition. During these experiments, the pressure is continuously monitored and is used to deduce significant events such as the end of compression and the onset of ignition. The pressure profile is also used to assess the temperature evolution of the gas mixture with time using the adiabatic core hypothesis and the heat capacity ratio of the gas mixture. In such RCM studies, real transportation fuels containing many components are often represented by simpler surrogate fuels. While simpler surrogates such as primary reference fuels (PRFs) and ternary primary reference fuel (TPRFs) can match research and motor octane number of transportation fuels, they may not accurately replicate thermodynamic properties (including heat capacity ratio). This non-conformity could exhibit significant discrepancies in the end of compression temperature, thereby affecting ignition delay (τ_{ign}) measurements. Another aspect of RCMs that can affect τ_{ign} measurement is post compression heat loss, which depends on various RCM parameters including geometry, extent of insulation, pre-heating temperature etc. To, better understand the effects of these non-chemical kinetic parameters on τ_{ign} , thermodynamic properties of a number of FACE G gasoline surrogates were calculated and simulated in a multi-zone RCM model. The problem was further investigated using a variance based analysis and individual sensitivities were calculated. This study highlights the effects on τ_{ign} from thermodynamic properties of various surrogate fuels and differences in post compression heat loss over low, intermediate and high temperature region.

Keywords: Ignition delay; surrogate formulation; rapid compression machine.

1. Introduction

Rapid compression machines (RCM) are routinely used to study autoignition of fuels under temperature and pressure of relevance to practical engines. A wide variety of fuels, ranging from pure hydrocarbons to regular gasoline and diesel [1-3] can be investigated in an RCM. Figure 1 describes a typical RCM experiment where a fuel/oxidizer mixture is rapidly compressed to top dead center (TDC) thereby reaching a higher pressure and temperature. After TDC, the compressed gases experience heat loss (manifested as pressure decay), which is followed by a small pressure rise marking the onset of first stage ignition. Further, second stage or final ignition is recorded by a sharp pressure rise, and this duration between TDC and final ignition is designated as ignition delay (τ_{ign}). In this experiment, two parameters are of particular significance for the accurate determination of τ_{ign} : 1) The fuel/oxidizer mixture's temperature at TDC (T_{TDC}); and 2) Post compression heat loss, manifested as pressure decay.

Figure 1: RCM pressure profile for a gasoline/air mixture at equivalence ratio $\phi = 1$ and $P_{TDC} = 20 \text{ bar}$ $T_{TDC} = 718 \text{ K}$ [3]

The effect of T_{TDC} on τ_{ign} is well known from several RCM studies [4-7] and also the effect of post compression heat loss on τ_{ign} is well understood [5]. Briefly, higher T_{TDC} increases the rate of

reactions promoting the ignition (except for negative temperature coefficient (NTC) region) and hence a shorter τ_{ign} is observed, while higher heat loss rate effectively reduces the bulk gas temperature thereby reducing the rate of reactions and yielding a longer τ_{ign} . Accurate temperature measurement in an RCM still remains a challenge, except for a few attempts [8-11]. The adiabatic core hypothesis [7] is largely used to estimate the temperature profile from the measured pressure trace. Equation 1 describes the relation between P_{TDC} , T_{TDC} of the adiabatic core and its dependence on γ , defined as the ratio of specific heats ($\frac{C_p}{C_v}$) of the fuel/oxidizer mixture.

$$\int_{T_1}^{T_2} \frac{\gamma}{\gamma-1} \frac{dT}{T} = \ln \left(\frac{P_2}{P_1} \right) \quad (1)$$

Equation 1 implies that γ needs to be well known to estimate T_{TDC} precisely. Figure 2 presents the effect of T_{TDC} on measured τ_{ign} in an RCM for iso-octane from the data set of Atef *et al.* at $P_{TDC} = 20$ bar and $T_{TDC} = 803, 841, 884K$. The measurements from these experiments demonstrate a reduction in τ_{ign} with increase in temperature, a well-known fact reiterated to substantiate the arguments in this study. In later sections, it is shown that the differences in T_{TDC} could be introduced by dissimilarities in γ of surrogates, in line with Eq. 1. Such surrogates could have identical ignition delays across a range of experimental conditions but due to the differences in γ , they could show dissimilarities in τ_{ign} in RCM.

It must be noted that differences in T_{TDC} in Fig. 2 are not due to dissimilar γ , but is attained through variation in initial experimental conditions and is presented solely to substantiate the effect of T_{TDC} on τ_{ign} .

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102

103 Figure 2: The effect of T_{TDC} on measured ignition delay for iso-octane in air at $\phi=1$ ($O_2: N_2 = 1:$
 104 3.76) at $P_{TDC}=20$ bar.

105

106 The implications of this observation lie in the practice of using surrogate fuels to represent
 107 transportation fuels in RCM simulations and experiments. Traditional surrogates for gasoline-type
 108 fuels are primary reference fuels (PRF) and ternary primary reference fuels (TPRF), which are
 109 comprised of iso-octane/n-heptane and iso-octane/n-heptane/toluene respectively. The PRFs and
 110 TPRFs are prepared to match research and motor octane numbers of the target fuel, while they do
 111 not necessarily match other fuel properties, including specific heat ratio (γ over the temperature
 112 range). If such discrepancies exists, they could introduce uncertainty in T_{TDC} , eventually affecting
 113 τ_{ign} measurements and simulations.

114 The other parameter considered in this study with a potential effect on τ_{ign} measurements in RCM
 115 is the post-compression heat loss which is specific to an RCM facility. In Fig. 3, RCM pressure
 116 traces from the National University of Galway, Ireland (NUIG) and the University of Connecticut,
 117 USA (UCONN), are shown under identical TDC conditions from the data set of Atef *et al.* [12]

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Figure 3: Comparison of RCM pressure traces from NUIG and UCONN under identical TDC conditions with iso-octane in air at $\phi = 1$ ($O_2: N_2 = 1: 3.76$) (Note: Initial mixture temperature was different in cases between $T_{TDC} \cong 740\text{ K}$ and 791 K)

In both the cases, measurements from UCONN show higher pressure decay, indicating higher rate of heat loss, and hence a longer τ_{ign} . Figure 3 interestingly points out that even under identical experimental conditions, different heat loss attributes of the RCM facility can result in different ignition delays for identical fuel/oxidizer mixtures. This observation also implies that, while studying a fuel across RCM facilities, the data must be interpreted in conjunction with the employed RCM's heat loss attributes, as earlier discussed by Mittal and Sung [7].

RCM exhibits a complex reactive flow problem, and there are several experimental factors that could affect the processes leading to ignition. Apart from differences arising from γ , temperature in the RCM is affected by experimental factors such as pressure, fuel mixing procedure, and diagnostic measurements techniques as shown by Weber *et al.* [13]. They also show that the initial temperature and pressure are the major sources of uncertainty in T_{TDC} estimation. RCM experiments often use diluents in ignition studies which leads to differences in ignition delay measurements. Wulmer *et al.* [14] conducted such an investigation on shock tube and RCM with different diluent mixtures and concluded that ignition delay strongly depends on diluent's properties such as thermal conductivity,

thermal diffusivity and heat capacity. In a similar investigation, Wagnon *et al.* [12] discussed the effect of four different diluent gases: argon, nitrogen, water, and carbon dioxide, on ignition delay measurements for three different fuels in an RCM. The heat release rates and τ_{ign} were found to be sensitive to diluents; the study also discussed the significance of diluents on low-temperature kinetics. Recently Goldsborough *et al.* [5] conducted a detailed review of recent RCM studies and also discussed about parameters that could significantly affect τ_{ign} measurements and simulations in RCMs. Some of the earlier investigations (and comparisons in Fig. 3) have shown that the RCM heat loss affects the τ_{ign} [4, 15] measurements and different RCM facilities could report different values of τ_{ign} under identical experimental conditions. However, to the authors' knowledge none of the earlier studies have conducted a detailed analysis of such effects of variation in T_{TDC} (due to γ) and heat loss on τ_{ign} in RCM, and therefore a detailed investigation is warranted. To study this problem in detail, three surrogates of FACE G [16] gasoline with different γ resulting in different T_{TDC} are considered. The effect of heat loss on ignition delay has been accounted for by building a simplified multi-zone RCM model to allow variation in the heat loss rate for fuels with single and multi-stage ignition delays. Furthermore, a numerical experiment was designed with τ_{ign} as a function of T_{TDC} (a strong function of γ) and heat loss rates. Investigations were conducted with a variance based analysis to decouple the effects of these parameters on τ_{ign} and identify individual sensitivities.

2. Methodologies

2.1 Thermodynamics of fuel and surrogate mixtures

FACE G is a fully characterized, high research octane number (RON = 96.8) and high octane sensitivity (S = 11) gasoline with high percentages of iso-paraffins (38 mol %) and aromatics (32 mol %). A detailed description of various properties of FACE G is available in the literature [16,

17]. In this section, FACE G and its three surrogates were investigated for their thermodynamic properties and their subsequent effect on T_{TDC} . These three surrogates are PRF91.5 (primary reference fuel), TPRF-G (ternary primary reference fuel), and FGG-KAUST (a multicomponent surrogate fuel), as described in Sarathy *et al.* [16]

Thermodynamic properties were calculated for all the species in FACE G, FGG-KAUST, PRF91.5, and TPRF-G. In Table 1, temperature dependent heat capacities: C_{pT} , enthalpy of formation at 298 K: H_{f298} and entropy of formation at 298 K: S_{f298} , are shown for FACE G and surrogates. These calculations were made using the group additivity methodology [18] implemented in the THERM software [19] on CloudFlame portal (cloudflame.kaust.edu.sa) developed at KAUST [20, 21]. The calculations employ updated group values based on the work of Burke *et al.* [22]. The species formula, identification of groups, number of rotors and symmetry number were declared for each individual species for the computations. Finally, the thermodynamic properties for each species was multiplied by its mole fraction to obtain the final thermodynamic properties of the blend.

Thermodynamic properties for a few representative species found in the DHA of FACE G are also presented in Table 1. Also, heat capacity as a function of temperature, C_{pT} is presented for a large range of temperatures ($T = 300-900$ K). The last three rows of Table 1 (in bold) report thermodynamic properties calculated for FACE G, and its surrogates FGG-KAUST, TPRF-G and PRF91.5. A similar table, with the thermodynamic properties of all components in FACE G and surrogates, is given as Supplementary Material (file title: “FACE G and surrogates”). In Table 2, H/C ratio and molecular weight of FACE G and surrogates is reported.

Table 1: Thermodynamic properties of representative species from the DHA of FACE G. The last four rows (bold) report the respective properties, considering fuel and surrogates as mixtures of hydrocarbons. Thermodynamic properties are referred to a standard state of an ideal gas at 1 atm.

<i>Species</i>	^a <i>H</i> _{f298}	^b <i>S</i> _{f298}	^c <i>C</i> _{p300}	<i>C</i> _{p400}	<i>C</i> _{p500}	<i>C</i> _{p600}	<i>C</i> _{p700}	<i>C</i> _{p800}	<i>C</i> _{p900}
n-butane	-2.99E+04	7.34E+01	2.39E+01	2.96E+01	3.49E+01	3.97E+01	4.40E+01	4.77E+01	5.09E+01
i-pentane	-3.66E+04	8.19E+01	2.84E+01	3.62E+01	4.35E+01	5.00E+01	5.57E+01	6.05E+01	6.46E+01
2,2,4-trimethylpentane	-5.32E+04	1.01E+02	4.53E+01	5.83E+01	6.95E+01	7.90E+01	8.71E+01	9.40E+01	9.98E+01
m-xylene	3.81E+03	8.55E+01	3.05E+01	3.94E+01	4.76E+01	5.49E+01	6.11E+01	6.62E+01	7.04E+01
methylcyclopentane	-2.52E+04	8.09E+01	2.61E+01	3.57E+01	4.48E+01	5.28E+01	5.93E+01	6.44E+01	6.84E+01
1-pentene	-5.03E+03	8.27E+01	2.60E+01	3.30E+01	3.91E+01	4.44E+01	4.89E+01	5.29E+01	5.62E+01
-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-
FACE G	-2.42E+04	8.77E+01	3.30E+01	4.26E+01	5.13E+01	5.89E+01	6.55E+01	7.09E+01	7.54E+01
FGG-KAUST	-2.31E+04	8.73E+01	3.25E+01	4.19E+01	5.04E+01	5.78E+01	6.42E+01	6.96E+01	7.40E+01
TPRF-G	-1.02E+03	8.21E+01	2.88E+01	3.80E+01	4.58E+01	5.24E+01	5.78E+01	6.24E+01	6.62E+01
PRF91.5	-5.25E+04	1.01E+02	4.47E+01	5.76E+01	6.86E+01	7.80E+01	8.60E+01	9.27E+01	9.85E+01

^a Enthalpy of formation in Cal/mole, ^b entropy of formation in Cal/mol-K, ^c heat capacity in Cal/mol-K

Table 2: H/C ratio and Average molecular weight of FACE G and surrogates studied in this study

Properties	FACE G	PRF 91.5	TPRF-G	FGG-KAUST
H/C	1.83	2.25	1.4	1.85
Avg. mol. wt.	99.7	112.9	94.8	94.3

In Fig. 4, the heat capacity, C_p and specific heat ratio, γ for FACE G, FGG-KAUST, TPRF-G and PRF91.5 are compared at stoichiometry, $\phi = 1$, Fuel/air mixtures. The C_p and γ for FGG-KAUST match those of FACE G, which is also evident from Table 1. However, TPRF-G and PRF91.5 shows deviations averaging around 8 – 10 %.

Figure 4: Comparison of thermodynamic properties of air-fuel mixture at $\phi=1$ with fuel as FACE G (symbols), FGG-KAUST, TPRF-G and PRF91.5.(left), heat capacity, C_p , (right) ratio of heat capacity, γ .

This discrepancy in γ between FACE G and surrogates (PRF91.5 and TPRF-G) could lead to inconsistency in T_{TDC} in RCM experiments and simulations. Therefore to further investigate, Chemkin Pro [23] inert RCM simulations were conducted with PRF91.5, TPRF-G and FGG-KAUST. For these simulations, individual volumetric profiles were generated using fuel specific γ and pressure traces from Sarathy *et al.* [16] at equivalence ratio, $\phi = 1$ for inert mixtures (Fuel/ N_2 mixture). The comparison between temperature profiles of FGG-KAUST, TPRF-G and PRF91.5 is presented in Fig. 5 for two cases. Zoomed insets are also provided within respective figures to highlight the differences in the attained T_{TDC} .

Figure 5: Effect of γ on TDC temperature in two different cases for all the surrogates of FACE G, i.e., FGG-KAUST, TPRF-G, and PRF91.5 at $\phi=1$ and identical initial conditions.

FGG-KAUST closely emulates C_p and γ of FACE-G (see Fig. 4) and hence it is expected to closely match FACE G - T_{TDC} in RCM. FGG-KAUST (a multicomponent surrogate) provide improved reproduction of several target fuel properties such as H/C ratio, molecular weight (see Table 2), carbon types [24], RON, MON, volatility etc. [16, 25-29]. These well matched properties especially carbon types along with H/C ratio and molecular weight includes the complete structural description of the target fuel. Such a matching of properties eventually allows molecular level replication of the composition of the target fuel ensuring improved performance of the surrogate on multiple fronts, for example thermodynamic, properties in this case. It is also notable that PRF91.5 shows maximum deviation in C_p and γ from FACE G (see Fig. 4), which explains the highest difference in the T_{TDC} (15 K) from FGG-KAUST in Fig. 5.

Hence it is established that T_{TDC} is a strong function of heat capacities ratio, $\gamma (= \frac{C_p}{C_v})$; therefore in further discussion only T_{TDC} is analyzed and its subsequent effect on ignition delay is discussed.

2.2 RCM multi-zone model

To accurately assess the impact of post-compression heat loss on τ_{ign} , a multi zone model for RCM, similar to Zhang *et al.* [30] has been developed. This model is written in Python- Cantera [31] and allows simulation of ignition delay in RCMs with different rates of heat loss at diverse T_{TDC} . This model consists of three zones: **zone 1**) the adiabatic core, **zone 2**) the boundary layer and **zone 3**) the crevice, as shown in Fig. 6.

The assumptions involved in developing the model are as follows:

1. The zones are homogenous in concentration and temperature, and pressure is equivalent across all the zones.
2. During the compression phase, the dimensions of the adiabatic core and boundary layer zone (not present at the beginning of compression) decrease with time as the piston proceeds towards TDC. Post-compression, all the zone volumes are kept constant.
3. In accordance with adiabatic core hypothesis, the core zone is modeled as adiabatic. Heat loss is experienced only at the boundary layer zone and the crevice zone to the RCM wall.
4. The core zone is modeled as reactive, while the boundary layer and crevice zone are non-reactive.
5. Heat loss is only implemented in post-compression phase.

Figure 6: Schematic of multi-zone model for RCM with three zones 1) adiabatic core, 2) boundary layer and 3) crevice zone

In the current model, heat loss is implemented at the boundary layer and the crevice zone while the adiabatic core remains unaffected as discussed in Lee *et al.* [32]. The heat loss term is expressed as a polynomial function of temperature, surface area and time. Heat loss function was acquired empirically and is expressed as Eq. 2.

$$Q = (K_{BL}(T_{BL} - T_{wall})^n + K_{crevice}(T_{crevice} - T_{wall})^n)t_{TDC} \quad (2)$$

Where,

T_{BL} = temperature of boundary layer

$T_{crevice}$ = temperature of crevice

T_{wall} = temperature of RCM wall

t_{TDC} = time lapsed after TDC

The temperature of the homogenous non-reactive zones, boundary layer and crevice is calculated at each time step with evolving adiabatic core pressure and heat loss to the ambient. The constants K_{BL} and $K_{crevice}$ in the heat loss term consist of a calibration constant (representing convective heat transfer coefficient) and the annular surface area of the inner wall of RCM through which heat loss takes place to the ambient. The constant n is iteratively adjusted to match the pressure decay of the system across several inert RCM profiles.

In Fig. 7, the pressure decay calculated with the RCM model is shown against experimental pressure decay, for two different cases from Sarathy *et al.* [16], and fixed wall temperature of $T_{wall} = 340K$.

Figure 7: Post compression pressure decay for different TDC conditions in RCM model and experiments. P_exp presents the experimentally measured pressure history for an inert run. P_model is predicted by RCM multi-zone model

2.3 Numerical experiment: Mapping the effect of γ and heat loss on τ_{ign}

A numerical experiment was designed to evaluate the collective effect of these parameters on τ_{ign} in RCM. The objective of this exercise is to quantify the variance in ignition delay, with deviations in T_{TDC} representing different surrogate mixtures, and α , signifying diverse heat loss rates from

different RCM facilities. As previously noted, in RCM operations, fuels exhibit either single or two stage ignition; therefore, two different cases were considered in the current framework, representing single and two stage ignition events along with a broad range of heat loss rates. Variation in the ratio of heat capacities, γ from surrogates, is expressed in terms of T_{TDC} , whose range was selected to yield single and two stage ignition events. Further, the T_{TDC} range was parameterized using an independent distribution of a canonical random variable ξ_1 , uniformly distributed over $[-1,1]$, according to Eq. (3):

$$T_{TDC} = T_1 + \left(\frac{\xi_1+1}{2}\right)(T_2 - T_1) \quad (3)$$

Following the previous discussion, two temperature ranges were selected in single and two-stage ignition regions; the selected bounds were $T_1 = 808$ K, $T_2 = 868$ K and $T_1 = 730$ K, $T_2 = 790$ K respectively. The temperature ranges defined above were discretized with Eq. (3), and seven node points were obtained between T_1 and T_2 , in both cases representing a range of T_{TDC} .

To study the effect of post TDC heat loss on ignition delay, a heat loss factor α , was defined and parametrized using a second independent and identically distributed random variable, ξ_2 , as $\alpha = UF^{\xi_2}$. An uncertainty factor, $UF=2$, was assigned describing the variability in levels of heat loss from RCM facilities. The node points were located at $\xi_2 = \cos\left(\frac{k\pi}{M-1}\right)$ with $k = 0,1, \dots (M-1)$, equal to the number of nodes in the T_{TDC} interval. Here M is given as [33] $M = 2^{l(3)} - 1 = 7$, which is defined by the Clenshaw Curtis rule of level 3 ($l=3$). The range of ξ_2 defines the upper and lower bounds of heat loss, allowing variations from 0.5 to 2.0 for α . In the process, seven heat loss cases were generated, corresponding to each T_{TDC} point in both the temperature intervals, and representing single and two stage ignition cases, as shown in Table 3. The discrete values of T_{TDC} and α were considered over a two-dimensional space, and τ_{ign} was mapped for different combinations over this space, representing different surrogate mixtures and heat loss rates as shown in Table 3. Thus, a simulation experiment was established to ascertain the impact of T_{TDC} and heat loss rates on τ_{ign} .

Table 3: Heat loss factor and TDC temperature for the simulation exercise.

Heat Loss Factor, α	T_{TDC} -two stage (K)	T_{TDC} -single stage (K)
0.500	730	808
0.548	734	812
0.700	745	823
1.000	760	838
1.414	775	853
1.822	786	864
2.000	790	868

Apart from the conditions shown in Table 3, another case with adiabatic condition ($\alpha = 0$) was also considered to derive better understanding of effect of heat loss on ignition delay and will be discussed in later section.

3. Results and discussions

3.1 Effects of T_{TDC} and heat loss on τ_{ign}

Multi-zone RCM simulations were conducted using FGG-KAUST/air mixture at $\phi=1$ with the chemical kinetic mechanism from Sarathy *et al.* [16]. The compression segment of RCM was excluded, and simulations were initiated from TDC to ascertain pre-determined T_{TDC} values. This simplification prolonged the predicted τ_{ign} , as also shown by Mittal *et al.* [6]. In Fig. 8 (a) and 8 (b), cases for two and single stage ignition events corresponding to T_{TDC} range of 730-790 K and 808-868 K respectively, are presented. Comparing the trends in ignition delay observed in Fig. 8 (a) and 8 (b), τ_{ign} was found to be more sensitive to temperature in the lower temperature (LT) region (730-790 K). This observation is ascertained by steep slope of τ_{ign} in LT region in Fig. 9, a characteristic of high octane sensitivity fuels such as FACE G. The T_{TDC} range of 808-868 K lies in the NTC region, which significantly reduced the overall sensitivity of ignition delay to temperature within this interval. This observation implies that an accurate description of γ is imperative if the intended T_{TDC} lies in either the HT or LT region for high octane sensitivity fuels, while minor changes in T_{TDC}

are not significant to τ_{ign} in the NTC region. Furthermore, the NTC (Fig. 8 (b)) case with $T_{TDC}=808$ K demonstrates weak first stage ignition (temperature rise < 50 K) before final ignition. This event indicates shifting of fuel ignition behavior from the single to two stage ignition region, due to the shift in T_{TDC} . Thus, apart from introducing uncertainty in the τ_{ign} , poorly formulated surrogates may shift the ignition behavior from single- to two-stage ignition or vice versa especially when T_{TDC} lies near the turnover point.

Figure 8: The effect of T_{TDC} on ignition delay: (a) two-stage ignition corresponding to T_{TDC} range of 730-790 K (b) single stage ignition cases corresponding to T_{TDC} range of 808-868 K for FGG- KAUST $\phi = 1$

Figure 9: Ignition delay obtained from RCM multi-zone model for FGG-KAUST in air ($T_{TDC} = 730-868$ K at 20 bar, $\phi = 1$)

In Fig. 10 (a) and (b), the effect of heat loss on τ_{ign} is presented again for cases with two and single stage ignition events for $T_{TDC} = 730$ K and 868 K respectively. Heat loss rate was varied by multiplying by the heat loss term, Q (Eq. 2) by the heat loss factor, α during the simulations. Along with the cases shown in Table 3, another case with no heat loss ($\alpha = 0$) has been added to Fig. 10 (a) and (b). This case with no heat loss does not only shows significant decrease in final ignition delay time in both single- and two-stage ignition cases but also a reduction in interval between ignition events is observed.

Figure 10: RCM simulations showing the effect of heat loss on ignition delay (a) two-stage ignition events at $T_{TDC} = 730$ K (b) one stage ignition events at $T_{TDC} = 868$ K

Ignition delays in Fig. 10 (a) with non-zero ($\alpha \neq 0$) heat loss rates indicates that the effect of heat loss is only experienced by first stage ignition events, which are advanced or delayed based on employed heat loss factor, indicated by α . Second stage ignition however, remains virtually unaffected within the range of heat loss variation in this study. This occurrence could be explained by the steep temperature rise rate after the first-stage ignition event up to the final ignition; such a high rate of heat release effectively mitigates the impact of heat loss and thus the interval between the first and second stage ignition events remain unchanged. Figure 10 (b), presents another set of RCM simulations with $T_{TDC} = 868$ K and the effect of heat loss on single-stage ignition events. The increasing rate of heat loss is shown to prolong the ignition delay time, however the change observed in ignition delay due to the effect of heat loss variation is quantitatively and qualitatively similar in both cases (Fig. 10 (a) and 10 (b)) across the range of α . To further investigate the effect of heat loss on the interval between first and second stage ignition events, an additional set of simulations were conducted for FACE G at $\phi = 0.5$ with 90 % N_2 dilution at $T_{TDC} = 670$ K and 20 bar, as shown in Fig. 11. The range of heat loss rates extended from no heat loss ($\alpha = 0$) to double the heat loss ($\alpha =$

2) of the nominal case. These conditions showing a longer interval between first and second stage ignition events were specifically selected to investigate the effect of heat loss on this duration ($\tau_2 - \tau_1$).

Figure 11: RCM simulations showing the effect of heat loss on ignition delay (a) two-stage ignition events at $\phi = 0.5$ with 90 % dilution with N_2 at $T_{TDC} = 670$ K and 20 bar

The effect of heat loss on first stage ignition in Fig. 11 is qualitatively similar to Fig. 10 (a), first stage ignition is delayed by increasing the rate of heat loss. Further analyzing the interval between the first and second stage ignition events indicate that the second stage ignition events are also marginally delayed in cases with higher heat loss rates. Another case with no heat loss is also presented in Fig. 11, which shows significantly shorter first and second stage ignition events. A note should be taken about the time span of these ignition delays, the first ignition delay is observed around 200 msec, and the final ignition takes place at approximately 800 msec. The magnitude of second stage ignition event is well above the practical test time limit for experimental RCM facility and attaining such conditions in the laboratory would be highly unlikely. However, this trend indicates that the effect of heat loss on second stage ignition events could be observed in cases with significantly higher τ_{ign} .

Figure 12 shows the ignition delay profile for the entire temperature range (730-868 K) across the range of heat loss factors ($\alpha = 0$ to 2.0). The increment in heat loss rates is shown to introduce an

increment in τ_{ign} , which is also reflected in Fig. 3, while comparing τ_{ign} from NUIG and UCONN RCMs. Also as earlier seen in Fig. 10 (b), alterations in heat loss rates introduces a shift in the turnover point between HT, LT and NTC region; at lower heat loss rates the turnover point is attained at lower T_{TDC} due to higher bulk gas temperature.

Figure 12: Change in ignition delay due to variation of heat loss factor over the temperature range of 730-868 K

3.2. Variance analysis

Variance analysis was conducted to quantify the combined impact of the variability in T_{TDC} and the heat loss factor, α , on τ_{ign} , and to identify individual sensitivities of these factors on τ_{ign} . As previously discussed in section 2.3, the T_{TDC} and the heat loss factor α were parameterized using random variables ξ_1 and ξ_2 respectively, signifying variance in T_{TDC} and heat loss rates. A polynomial chaos (PC) formalism was used to represent the dependence of τ_{ign} on the uncertain inputs. Specifically, τ_{ign} is expressed [33, 34] as : $\tau_{ign}(\xi) = \sum_{k=0}^P c_k \psi_k(\xi)$

where Ψ_k is a multidimensional Legendre polynomial in : $\xi = (\xi_1, \xi_2)$, and $P + 1$ is the size of the basis, truncated to retain polynomials of total degree less, or equal to, three. To determine the unknown coefficients, a regularized regression technique was used [34, 35]. The computation of τ_{ign} at selected realizations of ξ was used for this purpose. A fully tensorized grid with seven values of ξ_1 was used, those yielding the T_{TDC} values determined for the different mixtures considered with different γ , and seven values of ξ_2 , coinciding with the nodes of a third-level Clenshaw-Curtis quadrature rule [36] for different heat loss rates. The response surface generated for $T_{TDC}= 730-790$ K is presented in Fig. 13. Observations from Fig. 13 are discussed, along with Fig. 14 in the following section.

Figure 13: PC response surface with individual realizations for range, $T_{TDC}=730-790$ K. Right Corner: First order and total sensitivity indices indicating dependence of τ_{ign} on temperature and heat loss factor

Figure 14 shows a similar PC response surface, with individual realizations for the temperature range $T_{TDC} = 808 - 868K$. The temperature range considered for this formalism includes the NTC ignition region and as expected τ_{ign} initially increased and then decreased with rising T_{TDC} .

Figure 14: PC response surface showing dependence of τ_{ign} on T_{TDC} and α with $T_{TDC} = 808 - 868K$. Right Corner: First order and total sensitivity indices indicating dependence of τ_{ign} on temperature and heat loss factor

To quantify the variability in τ_{ign} , first and total order sensitivity indices were computed as shown in Fig. 13 (right corner) and Figure 14 (right corner). First order sensitivity indices, S_1 and S_2 , respectively account for the direct contribution of ξ_1 and ξ_2 to the variance in τ_{ign} ; total sensitivity indices, T_1 and T_2 , also account for the mixed effects. All quantities can be readily computed from the PC coefficients, c_k [27]

The first order (S_i) and total order (T_i) sensitivity indices shown in Fig. 13 and 14 are calculated using Eq. (4) and (5):

$$S_i = \frac{\sum_{k \in S_i} c_k^2 \|\psi_k\|_{L_2}^2}{\sum_{k=1}^{\infty} c_k^2 \|\psi_k\|_{L_2}^2} \quad (4)$$

Where, $S_i = \{k \mid \psi_k \text{ has degree } 0 \text{ in all } \xi_j \text{ with } j \notin i\}$
 $i \in \{1, \dots, d\}$ and d is the dimension

$$T_i = \frac{\sum_{k \in T_i} c_k^2 \|\psi_k\|_{L_2}^2}{\sum_{k=1}^{\infty} c_k^2 \|\psi_k\|_{L_2}^2} \quad (5)$$

Where, $T_i = \{k \mid \psi_k \text{ has degree } > 0 \text{ in all } \xi_j \text{ with } j \in i\}$

In Fig. 13 (right corner) the sensitivities of τ_{ign} to T_{TDC} were substantially higher than those associated with the heat loss factor. This occurrence could be attributed to the temperature region 730-790 K, where the ignition delay shows steep change with temperature, as also shown in Figure 9. Such high dependence on temperature in this region offsets the effect of heat loss and shifts first and total order sensitivity of τ_{ign} towards T_{TDC} . Note also that the first order total sensitivity indices achieved very close values, indicating that mixed interactions between T_{TDC} and α are weak.

In Fig. 14, the sensitivities of τ_{ign} to T_{TDC} and α were comparable in magnitude, showing a higher effect of heat loss rate on τ_{ign} compared to T_{TDC} . This shift in sensitivity from Fig. 13 could be explained by a lesser dependence of ignition delay on temperature due to NTC behavior in the temperature range involved. The range of temperatures covered in this study included regions showing low temperatures and NTC region of ignition. High temperature ignition displays strong dependence on temperature, similar to ignition in low temperature regions, therefore similar sensitivities are expected to be observed.

4. Summary and Conclusions

The purpose of this study is to investigate the effect on ignition delay measurements and simulations in RCM due to discrepancies in T_{TDC} by using surrogate fuels with different heat capacity ratios (γ) and also due to using RCM facilities with diverse heat loss rates. To this end, thermodynamic

properties were determined for gasoline FACE G and surrogates using group additivity calculations for each of its constituents. The thermodynamic properties of FACE G were compared against the surrogate mixtures PRF91.5, TPRF-G and FGG-KAUST to explain discrepancies in the attained T_{TDC} in an RCM under identical experimental conditions. It was also shown that the multi-component surrogate (FGG-KAUST) better emulates heat capacity ratio (γ) of FACE G compared to simpler PRF or TPRF surrogate mixtures and hence would closely predict FACE G- T_{TDC} . The difference in T_{TDC} arising due to surrogates with inaccurate γ was shown to have implications on ignition delay times determined in RCMs. Post compression heat loss in RCMs is considered to be the second factor to effect ignition delay, which is dependent on the RCM facility's geometry (piston, volume to surface ratio), level of insulation, and wall temperature etc. The implications of heat loss rates on ignition delay are also presented which compares pressure traces from two different RCMs (Fig. 3).

Furthermore, a simplified multi-zone RCM model was developed and was used to analyze trends in ignition delay due to the combined effects of variation in heat loss and differences in T_{TDC} due to γ . A numerical experiment was then devised and ignition delays were sampled at several nodes, representing different surrogate mixtures and RCM facilities. In addition, variance analysis was performed and sensitivities were calculated to quantify the effect of T_{TDC} and heat loss rate on ignition delay in RCM.

The main conclusions drawn from this study are:

- Multicomponent surrogate mixtures are found to better emulate thermodynamic properties due to improved matching of H/C ratio, molecular weight, and carbon types along with several other chemical and physical properties with the target fuel. Better matching of thermodynamic properties ensures precise estimation of T_{TDC} and minimizes discrepancies in the acquired ignition delay data.

- Heat capacity ratio (γ), (determining T_{TDC}) has a greater effect on ignition delay than the heat loss rate (α) in low and high temperature regions due to higher sensitivity of ignition delay to temperature in these regions.
- For high sensitivity fuels such as FACE G, change in ignition delay with temperature is relatively smaller in the NTC region than in the high and low-temperature regions. Therefore, in the NTC region, the effect of heat loss rate on ignition delay is nearly comparable to the effect of temperature on ignition delay.
- The employed surrogate fuel could shift the ignition delay curve on the temperature axis due to discrepancy in the attained T_{TDC} . This shift would be entirely driven by thermodynamics of the surrogate fuel mixture.
- Surrogates with poorly matching of thermodynamic properties may shift fuel ignition behavior from the single to two-stage ignition region, due to the shift in T_{TDC} . Thus, apart from introducing uncertainty in ignition delay measurement, poorly formulated surrogates may artificially shift the ignition behavior from single to two-stage ignition or vice versa especially when T_{TDC} lies near the turnover point.
- In cases with two-stage ignition events, the first-stage ignition experiences delay when higher heat loss rates are considered. The time interval between first-stage and second stage ignition remained relatively constant as heat loss rate was varied except for cases with significantly higher second stage ignition delays.

Acknowledgments

Research reported in this paper was funded by Saudi Aramco under the FUELCOM program and by King Abdullah University of Science and Technology (KAUST). The authors also acknowledge the

informative discussions with Dr. Tamour Javed at Fuel Technology Team, Research and Development Center Aramco, Dhahran, Kingdom of Saudi Arabia.

Supplementary material

Supplementary material is provided, with figures and tables to support the work.

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