

13th U. S. National Combustion Meeting
Organized by the Central States Section of the Combustion Institute
March 19–22, 2022
College Station, Texas

Compositional effect of multi-component gasoline on the ϕ -sensitivity of ignition delay time

Jaeyoung Cho^{1,2}, Song Cheng^{1,3}, S. Scott Goldsborough¹, Seonah Kim^{2,4,*}

¹ Argonne National Laboratory, 9700 S Cass Ave, Lemont, IL 60439, USA

² National Renewable Energy Laboratory, 15013 Denver W Pkwy, Golden, CO 80401, USA

³ The Hong Kong Polytechnic University, 11 Yuk Choi Rd, Hung Hom, Hong Kong

⁴ Colorado State University, Fort Collins, CO 80523, USA

* Corresponding Author Email: seonah.kim@colostate.edu

Abstract: The ϕ -sensitivity (η) of ignition delay times (τ) has been recognized as an important fuel property for suppressing the abrupt pressure rise in advanced compression ignition engines. Despite several efforts to predict the η of single compound fuels, the compositional effects of multi-component fuels on their η are less known. In this regard, this study analyzed the η of multi-component fuels based on the experiment-modeling combined approaches. Five multi-component gasoline (CoOptima fuels) with different distributions of PIONA (paraffin, *iso*-paraffin, olefin, naphthene, and aromatic) and ethanol content were selected as representative fuels, all of which have a comparable research octane number (RON). The rapid compression machine (RCM) data from the literature (Kang et al., *SAE Technical Paper*, 2019) on the selected fuels were utilized to evaluate their η at intermediate-temperature chemistry regime (880 – 1000 K, 15 – 80 bar, ϕ of 0.28 – 0.38, and the diluent/O₂ ratio of 4.4). Interestingly, the selected fuels showed a similar η despite the vastly different composition, while the paraffin-dominated fuel (CoOptima Alkylate) with the lowest octane sensitivity (OS) exhibited a slightly elevated η at around 880 K and 80 bar. For further analysis, the 0-D simulation using the detailed kinetic model was conducted for the surrogate fuels matching the RON, OS, and distribution of PIONA/ethanol content of CoOptima fuels. The 0-D simulation showed the remarkable accuracy of τ prediction at both leaner ($\phi = 0.28$) and richer ($\phi = 0.38$) conditions. However, the η were poorly reproduced from the kinetic simulation, which may indicate the failure of surrogate fuels or kinetic mechanism. Further analysis on the η of 55 different single compound fuels revealed that the η is correlated ($R^2 = 0.773$) with the τ and the intermediate-temperature heat release (ITHR), where the former is related to the RON while the latter is known to correlate with OS. Therefore, we postulated that the compositional effect of multi-component fuels is minimal under the fixed RON and OS if the number of species in the fuel is sufficiently large, which explains the similar η of CoOptima multi-component gasoline despite their vastly different distributions of PIONA and ethanol content. This study provides the first systematic analysis of the compositional effect of multi-component fuels on the ϕ -sensitivity that can help the rational design of high-performance fuels for advanced propulsion systems.

Keywords: Chemical kinetics, Rapid compression machine, Compositional effect, ϕ -sensitivity

1. Introduction

Low-temperature gasoline combustion (LTGC) is one of the promising technologies for improving the emission and efficiency of medium-to-heavy-duty vehicles [1, 2]. LTGC features a low flame temperature and long ignition delay time, the former of which is beneficial to suppressing the thermal NO_x formation, while the latter guarantees the sufficient mixing time of

the fuel-air mixture reducing the particulate matter emission. Still, the high-load operation of the LTGC engine is limited by a high-pressure rise rate (PRR_{max}) during the autoignitive combustion process, eventually leading to shock wave propagation damaging the engine piston and liner.

In this regard, there have been several efforts to reduce the PRR_{max} in the LTGC engine. Dec et al. [3] proposed a stratified combustion strategy, where the extent of inhomogeneity of the fuel-air mixture is controlled by varying the portion of fuel mass injected in two different methods: port injection and direct injection. They revealed that the increased inhomogeneity spread out the instant of autoignition occurrence, contributing to the lower PRR_{max} . An additional simulation on the LTGC combustion showed that the sensitivity of fuel's ignition delay time (τ) to the equivalence ratio (ϕ), called ϕ -sensitivity, is one of the key fuel properties controlling the PRR_{max} in the LTGC engine [3, 4].

López-Pintor et al. [5] studied the ϕ -sensitivity of common gasoline surrogate fuels: *iso*-octane, *n*-heptane, toluene, and ethanol. They defined a normalized ϕ -sensitivity as $-\partial \log \tau / \partial \phi|_{T,P}$, which is positive in most engine operating conditions. Their chemical kinetics simulation showed that the normalized ϕ -sensitivity increases at the negative temperature chemistry (NTC) regime, making the fuel with two-staged ignition behavior prominent candidates for PRR_{max} suppression. Moreover, they revealed that the normalized ϕ -sensitivity is related to the intermediate temperature heat release (ITHR), which is governed by the hydrogen abstraction from the formaldehyde (CH_2O) and subsequent unimolecular/bimolecular reaction of formyl radical (HCO) producing HO_2 radical, followed by formation and dissociation of H_2O_2 .

Meanwhile, Messerly et al. [6, 7] executed the experiment-theory combined approach to further understand how the molecular structure affects the ϕ -sensitivity. They measured the ϕ -sensitivity of various single compound fuels (*iso*-octane, 2,4-dimethyl pentane, di-*iso*-propyl ether) using the Advanced Fuel Ignition Delay Analyzer (AFIDA). They defined the ϕ -sensitivity as $-\partial \log \tau / \partial \log \phi|_{T,P}$, which is equivalent to the ϕ 's exponent (η) in a typical form of empirical τ expression as a function of T , P , and ϕ ; e.g., $\tau = A\phi^\eta P^a \exp(-E_a/RT)$ [8-10]. The experimental results indicated that the kinetics model well-reproduces η of various fuels, enabling the deeper analysis ϕ -sensitivity from a mechanistic point of view. They found that the structural effect of η originates from the low-temperature chemistry: $RO_2 = QOOH$ isomerization, followed by the O_2 addition reaction $QOOH + O_2 = O_2QOOH$ and ketohydroperoxide (KHP) formation $O_2QOOH = KHP + OH$. Further analysis using quantum mechanics calculation showed the energy barrier of the $RO_2 = QOOH$ isomerization and the KHP dissociation are lowered with the ether-functional groups and branched structure, suggesting the *iso*-propyl propyl ether as a promising fuel candidate with high ϕ -sensitivity. Similar approaches using the AFIDA experiment were utilized by Cho et al. [11] to characterize the impact of dilution (e.g., exhaust gas recirculation) on the ϕ -sensitivity of *iso*-octane.

When it comes to multi-component fuels, López-Pintor et al. [5] designed high-performance multi-component fuels tailored for LTGC engines. They utilized the 0-D engine simulation with a detailed kinetics mechanism to formulate the optimal fuel composition. Two multi-component gasoline-like fuels were recognized as feasible with the improved research octane number (RON) and octane sensitivity (OS), as well as showing a high ϕ -sensitivity at the low-and-medium load operation. Their follow-up experimental studies [12, 13] validated that the suggested fuel with high ϕ -sensitivity effectively reduces PRR_{max} in the LTGC engine. Meanwhile, Kang et al. [14] measured τ of various multi-component gasoline-like fuels (so-called CoOptima fuels) using a rapid compression machine (RCM) at two different ϕ (0.28 and 0.38) with varying temperatures and pressure (880 – 1000 K, and 15 – 80 bar). They provided a comprehensive discussion on the

effect of each PIONA component (*n*-paraffine, *iso*-paraffine, olefin, naphthene, and aromatic) and ethanol content on τ of multi-component fuels, while paying less attention on these fuel's ϕ -sensitivity and their sensitivity to fuel composition.

The present study is an extension of Kang et al.'s effort to understand the ϕ -sensitivity of multi-component fuels with varying compositions based on the experiment-modeling combined approach. First, we re-analyzed the experimental τ of CoOptima fuels from Kang et al.'s RCM experiment to evaluate their η at engine-relevant conditions. Despite the vastly different compositions, we found out that η of the tested fuels are almost invariant if the RON and OS are fixed. The experimental results were then compared to the 0-dimensional (0-D) kinetics simulation using surrogate fuels; however, the kinetics model using surrogate fuels does not adequately reproduce the compositional effect of real fuels on their ϕ -sensitivity, which can be attributed to the missing chemistry in kinetics model or the failure of surrogate fuel formulation in ϕ -sensitivity representation. The experimental findings led us to postulate that η is mostly determined by the RON and OS of multi-component fuels, while its sensitivity to fuel composition becomes marginal as the number of components in the fuel increases. We supported our arguments through statistical analysis with extensive 0-D simulations for various single compounds fuels. This study is the first to analyze the compositional effect of multi-component fuels on ϕ -sensitivity, which is expected to deliver the comprehensive knowledge that guides alternative fuel design for LTGC engines.

2. Methodology

2.1. Rapid Compression Machine

The present study utilized the experimental data from Kang et al. [14] based on a heated, twin-piston RCM (tpRCM) at Argonne National Laboratory (ANL). A detailed description of the configuration, as well as uncertainties associated with experimental measurements, can be found in [14-17] and are also briefly described herein. The reaction chamber, with an inner diameter of 50.8 mm, is located between the two compression cylinders, while the clearance height at the end of compression is nominally 25.5 mm. The geometric compression ratio (CR) is 12.1:1; however, the effective compression ratio, when taking into account the heat loss during the compression, ranges from 11.2:1 to 11.8:1 depending on compressed state conditions, primarily the compressed pressure (P_C) and diluent conditions. The time for full compression and the last 50% of pressure rise is approximately 15 – 18 ms and 1.9 – 2.0 ms, respectively. The dynamic pressure in the reaction chamber is measured using a flush-mounted Kistler 6045A-U20 pressure transducer calibrated to 250 bar, and coupled to a Kistler Type 5064 charge amplifier. The compressed temperature (T_C), τ , and heat release rates (HRR) are determined by post-processing recorded pressure traces.

A 5.6 L stainless steel tank is heated to ~ 70 °C and is used to prepare mixtures of fuel, diluents (Ar and N₂), and O₂. A pre-determined mass of liquid fuel is first introduced into the tank through a septum, and then high-purity gases are supplied into the tank in the sequence of Ar (99.9997%, Airgas), N₂ (99.9998%, Airgas) and O₂ (99.9997%, Airgas). After completion of each mixture preparation, the mixture in the tank is isolated for 45 minutes to mix diffusively. τ is measured at two fuel loading conditions of $\phi = 0.28$ and 0.38, which we simply refer to lean and rich conditions in the remaining part of the paper. Blends of N₂ and Ar are employed to cover the target range of compressed pressures, while the overall dilution ratio is maintained at diluent/O₂ = 4.4. The specification of CoOptima fuels is described in Table 1.

In order to ascertain the end of compression (t_0) and the extent of the heat loss during τ , a non-reactive test, wherein O₂ in the test mixture is replaced with N₂, is conducted for each reactive case. Figure 1 presents the representative reactive traces along with the associated non-reactive

Table 1: Specification of CoOptima fuels

Parameters	CoOptima Alkylate (AKY)	CoOptima Aromatic (A30)	CoOptima Ethanol (E30)	CoOptima Naphthene (N30)	CoOptima Olefin (O30)
RON [-]	98.0	98.1	97.4	97.8	98.3
MON [-]	96.6	87.8	86.6	86.9	87.9
H/C [-]	2.2	1.8	2.2	1.8	2.0
<i>n</i> -paraffine [vol. %]	3.0	8.2	12.9	8.3	12.0
<i>iso</i> -paraffine [vol. %]	96.1	39.6	30.4	32.3	45.2
olefin [vol. %]	0.1	4.5	5.6	1.6	26.5
naphthene [vol. %]	0.0	8.0	7.0	24.2	2.9
aromatic [vol. %]	0.7	39.8	13.8	33.7	13.4

trace for an A30 case, where alignment between the non-reactive and reactive traces prior to heat release events are excellent. τ is also highlighted in Fig. 1, along with the normalized HRR derived using the method proposed in [18].

Uncertainty analyses associated with ANL’s tpRCM were presented in [15, 19], using a linear propagation approach similar to [20]. The uncertainty in computed T_C is estimated at 1.0 – 1.5 % due to instrumentation imprecision and procedural uncertainties associated with mixture preparation, and an uncertainty of ± 0.4 ms is estimated for each ignition delay measurement to account for the improper alignment with the non-reacting traces.

2.2. Kinetics Simulation

The pressure traces from the RCM experiment were reproduced with the 0-D dimensional kinetics simulation using a CoOptima2020 kinetics model from Lawrence Livermore National Laboratory consisting of 4146 species and 18732 reactions [21]. The CoOptima2020 contains the low- to high-temperature chemistry of various *n*-paraffine, *iso*-paraffine, olefine, naphthene, aromatics, and oxygenates, providing the optimal platform for simulating the autoignition characteristics of multi-component fuels with varying composition. The compression stroke and the heat transfer of ANL’s tpRCM were simulated with the effective-volume profile method. Briefly, the effective-volume profile method assumes that the adiabatic core in the combustion chamber undergoes the isentropic expansion during the thermal boundary layer growth; thus, the pressure and temperature drop in the adiabatic core can be simply reproduced by the adiabatic expansion process with the effective-volume profiles, $V_{eff}(t)$, achieved by converting the pressure-time profile of non-reactive run to the volume-time profile under isentropic process assumption. All the kinetics simulations were conducted in the Cantera and Python environments [22].

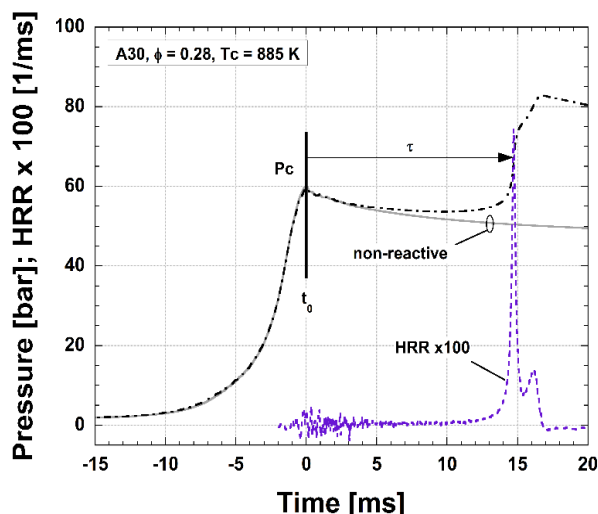


Figure 1. Representative experimental non-reacting and reacting pressure-time histories of A30 at $P_C = 60$ bar, $T_C = 885$ K with τ and HRR identified. HRR is normalized by LHV_{mix} .

Table 2: Specification of surrogate fuels (mol. %)

Parameters	Surrogate Alkylate (S-AKY)	Surrogate Aromatic (S-A30)	Surrogate Ethanol (S-E30)	Surrogate Naphthene (S-N30)	Surrogate Olefin (S-O30)
<i>n</i> -pentane	3.74	8.69	8.07	1.20	14.80
<i>n</i> -hexane	-	-	-	6.30	-
<i>iso</i> -pentane	-	7.92	21.85	18.60	4.50
<i>iso</i> -octane	94.48	25.27	1.37	9.40	36.20
toluene	-	24.74	-	21.80	4.20
1,2,4-trimethylbenzene	1.79	17.50	9.12	11.40	10.80
cyclopentane	-	11.59	7.24	29.80	4.40
1-hexene	-	4.29	4.13	1.40	3.80
2,4,4-trimethyl-2-pentene	-	-	-	-	21.20
ethanol	-	-	48.07	-	-

The multi-component gasoline contains thousands of species, where the accurate measurement of individual mole fractions is still challenging. Accordingly, the kinetics simulations of this study were conducted upon the surrogate multi-component fuels, which were formulated to reproduce the RON, OS, H/C ratio, and the relative ratios of each PIONA and ethanol component [23]. As shown in Table 2, *n*-paraffine and *iso*-paraffine components were represented with *n*-pentane/*n*-hexane and *iso*-pentane/*iso*-octane, respectively, where the ratios of different species were determined for best-reproducing the RON and OS of real fuels. Similarly, toluene and 1,2,4-trimethylbenzene were used to represent the aromatic components in the fuels, while cyclopentane was adopted as a representative of naphthene. Two olefinic components of *n*- and *iso*-alkene were selected as a representative of olefinic compounds, and the ethanol is also considered for simulating the E30.

3. Results and Discussion

3.1. CoOptima Alkylate

Figures 2(a) – 2(d) compare the simulated and experimental τ of AKY at lean and rich mixture. The experimental condition (880 – 1000 K and 15 – 80 bar) covers the typical operating conditions of LTGC engines [5], which is considered the intermediate temperature (IT) regime dominated by CH₂O and H₂O₂ chemistry. The measured τ of AKY spans 2 – 20 ms at the given conditions, and it monotonically depends on both temperature and pressure, except for the higher pressure (~80 bar) and low temperature (~880 K) region that falls into negative temperature coefficient (NTC) regime. The kinetics simulation of S-AKY properly reproduced the experimental τ at lean conditions with a relative average deviation (RAD) of 9.1 %. On the other hand, the τ at rich conditions were slightly underestimated with higher RAD of 20.0 %, whose impact can be propagated into the ϕ -sensitivity evaluation.

For further analysis of the ϕ -sensitivity, the experimental and simulated η were compared in Fig. 2(e) and 2(f), which are calculated at the condition where both lean and rich mixtures' τ maps were overlapped. The experimental data indicate that η of AKY is 1.28 on average at the given condition while it increases around ~80 bar and ~880 K (NTC regime), which is in line with the previous findings from the literature [5-7, 11] that showed the maximal η at NTC regime. The simulated η of S-ALK depicted a similar temperature and pressure dependency, increasing as getting closer to the NTC regime. However, the average η from the kinetics simulation is 1.85,

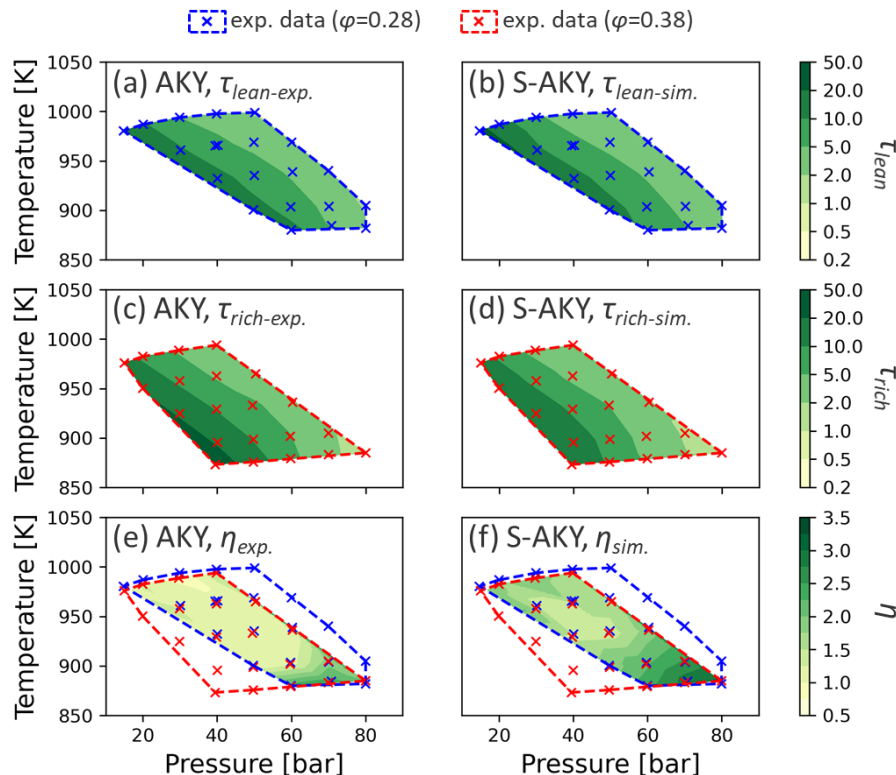


Figure 2. τ of ALK at $\phi = 0.28$ and 0.38 from (a, c) RCM experiment and (b, d) kinetics simulation. The (e) experimental and (f) simulated η of AKY were calculated at the overlap of T - P conditions of τ from lean and rich data.

significantly overestimating the experimental data despite the remarkable accuracy of τ at lean conditions. There can be multiple reasons for the discrepancy, which will be discussed in the following section.

3.2. Compositional effect on the ϕ -sensitivity

Analyses on the ϕ -sensitivity were then expanded to other CoOptima fuels (A30, E30, N30, and O30), which is shown in Fig. 3(a) – 3(j), including those of ALK as a reference. A30's η from experimental data indicates that the composition effect from aromatic contents, compared to ALK, is marginal at most of the tested conditions. However, A30 does not show the increasing η around low-temperature (~ 880 K) and high-pressure conditions (~ 80 bar). The absence of temperature-pressure dependency of A30's η may be related to the higher OS of A30 than AKY ($OS_{A30} = 10.3$ vs. $OS_{AKY} = 1.4$); that is, the high OS fuels exhibit minimal NTC behavior [24], which is known to be proportional to the fuels' η at low-temperature regime [5-7, 11]. The simulated η of S-A30 in Fig. 3(d) well-reproduces such a minimal temperature pressure dependency of experimental η of A30, with a slight overestimation of average η by 0.22 units at the given condition.

Figures 3(e), 3(g), and 3(i) depict the experimental η of E30, N30, and O30, respectively. All these fuels and A30 have comparable RON and OS (Table 1), and their η were also similar to each other despite the vastly different compositions. The average η of E30, N30, and O30 at the given conditions are around ~ 1.18 , showing a minimal temperature and pressure dependency owing to its high OS, as observed from A30. The simulated η of S-E30 and S-N30 in Fig. 3(h) and 3(j)

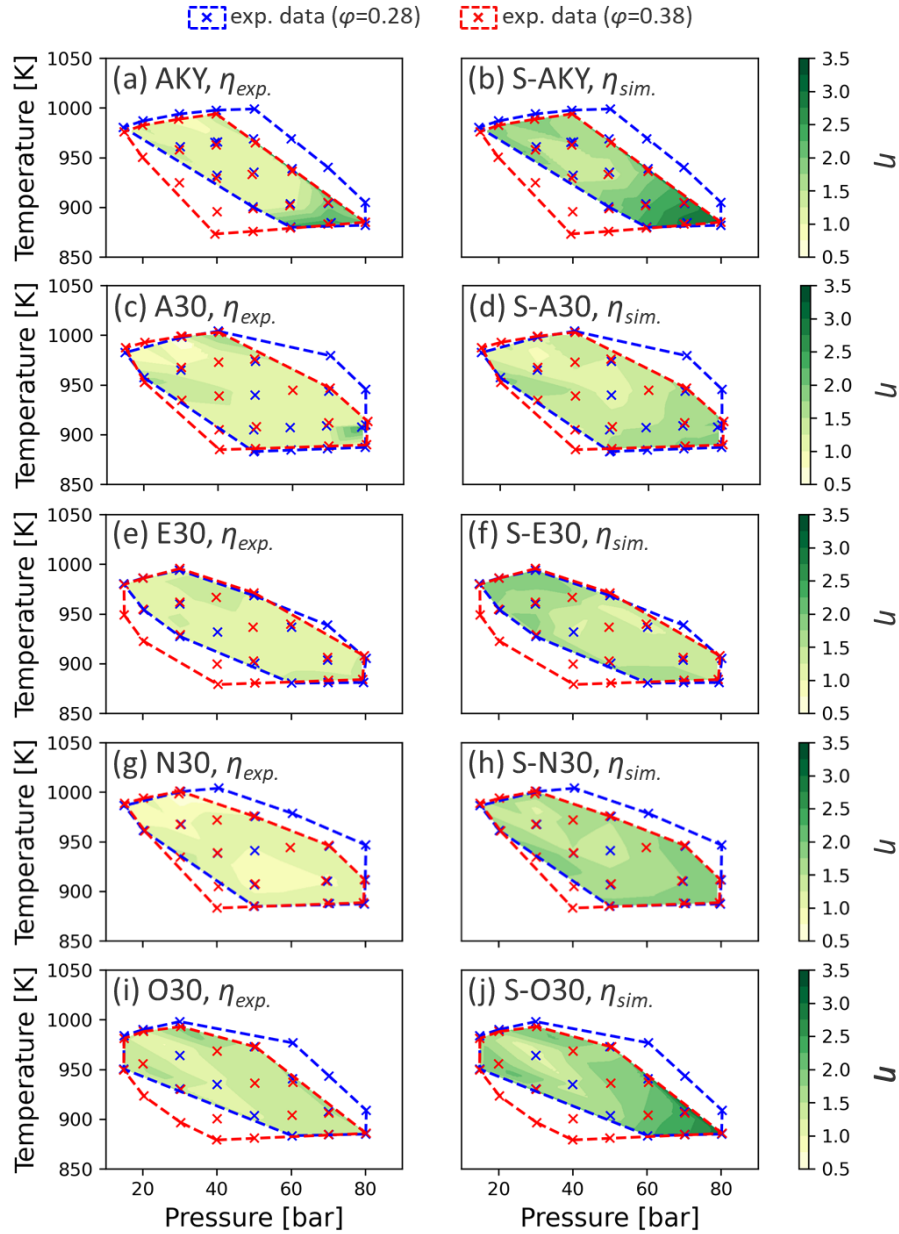


Figure 3. ϕ -sensitivity of five CoOptima gasoline fuels – (a) ALK, (b) E30, (c) O30, (d) A30, and (e) N30 – from RCM experiment and kinetics simulation. (f) Parity of kinetics model for the ϕ -sensitivity prediction.

well-reproduce the temperature and pressure dependency of experimental η while overestimating the average η by 0.32 unit and 0.60 unit, respectively. The simulated η of S-O30 increases with the higher pressure and lower temperature, reaching 3.04 at 884 K and 80 bar, which is inadequate for O30 having minimal NTC behavior. Moreover, the average η of O30 at the tested conditions is overestimated by 0.42 units. In summary, Fig. 3 indicates that the experimental η of CoOptima fuels have the minimal sensitivity to the PIONA distribution if the RON and OS are constrained (A30, E30, N30, and O30), while the η of low OS fuel (AKY) depicts high sensitivity to

temperature and pressure. However, the simulated η of the surrogate fuels poorly reproduces the experimental data, showing higher sensitivity to the PIONA composition.

The significant discrepancy between the experimental and simulated η can be attributed to two aspects. First, the kinetics model may fail to reproduce η owing to the uncertainties of the kinetics parameters or missing reactions. Especially at $\phi = 0.28$ and 0.38 , the kinetics model has rarely been validated, so the key reaction steps relevant to η can be missing. Second, the surrogate fuels may fail to represent the η of the CoOptima fuels. All the surrogate fuels described in Table 2 were formulated to reproduce only RON, OS, H/C ratio, and PIONA of CoOptima fuels, which does not necessarily mean they can simulate η too. Especially, the kinetics simulation on S-O30 showed a RAD of 41.6 % compared to the experimental τ of O30, leading to a huge discrepancy in η , which can be attributed to the uncertainty in either the kinetics model or surrogate fuel formulation.

3.4. Underlying physics determining the multi-component fuels' ϕ -sensitivity

As mentioned earlier, Fig. 3 might indicate the negligible impact of fuel composition on the multi-component fuels' η under a fixed RON and OS. For further verification, we conducted the kinetics simulation on η of 55 single compound fuels at 950 K, 50 bar, ϕ of 0.28 – 0.38, and diluent/O₂ ratio of 4.4. As depicted in Fig. 4, the η of selected fuels are distributed from 0.28 – 2.07, where the oxygenate compounds showed the most diverged distribution, followed by paraffin, olefin, naphthene, and aromatic.

To examine the correlation between η and octane numbers, we selected two parameters related to the RON and OS. The first is $\log(\tau)$; obviously, it is directly related to the octane number. The $\log(\tau)$ of each fuel was evaluated at 950 K and 50 bar to be consistent with RCM experiment conditions in previous sections. The second parameter is the intermediate temperature heat release (ITHR) characteristics, as several studies [25, 26] indicate that there is a close correlation between ITHR and OS. The present study used the temporal average of $(T(t)-T_0)$ during autoignition at IT regime (950 K and 50 bar), ΔT_{IT} , as a representative of ITHR characteristics.

We fitted η_i of each single compound fuel as a function of their $\log(\tau_i)$ and $\Delta T_{IT,i}$ using multivariate linear regression. As shown in Fig. 4, the derived equation, Eq (1), reproduces η_i with remarkable accuracy ($R^2 = 0.773$). The best-fit value of a_0 , a_1 , and a_2 were 0.0064, -0.1036, and 0.0059 K^{-1} , respectively, and the residual of regression, ϵ_i , follows the normal distribution with a standard deviation (σ) of 0.13.

$$\eta_i = a_0 + a_1 \log \tau_i + a_2 \Delta T_{IT,i} + \epsilon_i \quad (1)$$

, where $\epsilon_i \sim N(0, \sigma^2)$

As mentioned above, the $\log(\tau)$ and ΔT_{IT} are closely related to RON and OS; thus, Eq. (1) implies that the η_i of single compound fuels at IT regime is mostly determined by their RON_i and OS_i , with some unexplained degrees of freedom represented by ϵ_i . As we expand it to multi-component fuels, we can expect that $\eta_{\text{multi-comp.}}$ is still a function of $\log(\tau_{\text{multi-comp.}})$ and $\Delta T_{IT,\text{multi-comp.}}$ and dependent on the $\text{RON}_{\text{multi-comp.}}$ and $\text{OS}_{\text{multi-comp.}}$.

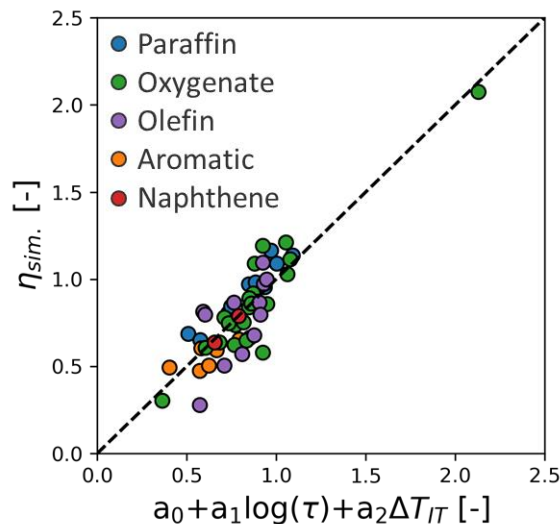


Figure 4. The correlation between η , $\log(\tau)$, and ΔT_{IT} of 55 single compound fuels

of multi-component fuel, as we observed in Fig. 3. Meanwhile, $\varepsilon_{multi-comp.}$ for multi-component fuels may have a smaller standard deviation than σ as the effect of each component's ε_i in the multi-component fuels will be canceled out. In other words, $\eta_{multi-comp.}$ of multi-component fuels will be more strongly dependent on the $RON_{multi-comp.}$ and $OS_{multi-comp.}$ with a minimal effect of other parameters, such as composition, LHV, etc. Although Fig. 4 gives us only a qualitative understanding of multi-component fuels' η , this analysis combined with the experimental evidence (Fig. 3) strongly suggests the minimal extent of compositional effects in the IT regime.

4. Conclusions

The present study analyzed the compositional effects on the ϕ -sensitivity of multi-component fuel based on the experiment-modeling combined approach. The ignition delay data of five CoOptima fuels with varying compositions from Kang et al.'s RCM experiment [14] were re-analyzed to evaluate their ϕ -sensitivity at the IT regime. CoOptima AKY, which is dominated by paraffinic compounds, shows even distribution η values around 1.28 except for the low-temperature and high-pressure conditions (880 K and 80 bar), where the NTC behavior is expected. The other CoOptima fuels with varying aromatic, ethanol, naphthene, and olefin fractions – A30, E30, N30, and O30 – depicted similar η 's of ~ 1.18 at the given condition. However, the kinetics simulation using surrogate fuels does not adequately reproduce η of the tested fuel, overestimating by up to 0.6 units or skewing its temperature and pressure dependency, which may suggest the missing reactions in the kinetics model or the misrepresentation of surrogate fuels. Consequently, the experimental data for five tested fuels indicates the minimal extent of composition effect on the ϕ -sensitivity under the fixed RON and OS. Further analysis for η of various single compound fuels revealed that η at the IT regime is strongly dependent on the ignition delay, $\log(\tau)$, and its ITHR characteristics, ΔT_{IT} , which are related to the RON and OS.

5. Acknowledgements

This research was conducted as part of the Co-Optimization of Fuels & Engines (Co-Optima) project sponsored by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy Bioenergy Technologies Office and Vehicle Technologies Office. Co-Optima is a collaborative project of several national laboratories initiated to accelerate the introduction of affordable, scalable, and sustainable biofuels and high-efficiency, low-emission vehicle engines. Work at the National Renewable Energy Laboratory was performed under Contract No. DE-AC36-08GO28308. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work or allow others to do so, for the U.S. Government purposes. Computer time was provided by the National Renewable Energy Laboratory Computational Science Center. The authors thank program manager Kevin Stork at the DOE Vehicle Technologies Office for supporting this research under the Co-Optima project.

6. References

- [1] J.E. Dec, J. Dornotte, C. Ji, Increasing the load range, load-to-boost ratio, and efficiency of low-temperature gasoline combustion (LTGC) engines, *SAE Int. J. Engines* 10 (2017) 1256-1274.
- [2] J. Dornotte, J.E. Dec, C. Ji, Energy distribution analysis in boosted HCCI-like/LTGC engines-understanding the trade-offs to maximize the thermal efficiency, *SAE Int. J. Engines* 8 (2015) 956-980.

Sub Topic: Alternative Fuels and Emissions

- [3] J.E. Dec, Y. Yang, N. Dronniou, Boosted HCCI-controlling pressure-rise rates for performance improvements using partial fuel stratification with conventional gasoline, *SAE Int. J. Engines* 4 (2011) 1169-1189.
- [4] M. Sjöberg, J.E. Dec, Smoothing HCCI heat-release rates using partial fuel stratification with two-stage ignition fuels, *SAE Int. J. Engines* 115 (2006) 318-334.
- [5] D. López-Pintor, J. Dec, G. Gentz, ϕ -sensitivity for LTGC engines: Understanding the fundamentals and tailoring fuel blends to maximize this property, *SAE Tech. Pap.*, 2019-01-0961.
- [6] R.A. Messerly, J.H. Luecke, P.C.S. John, B.D. Etz, Y. Kim, B.T. Zigler, R.L. McCormick, S. Kim, Understanding how chemical structure affects ignition-delay-time ϕ -sensitivity, *Combust. Flame* 225 (2021) 377-387.
- [7] R.A. Messerly, M.J. Rahimi, P.C.S. John, J.H. Luecke, J.-W. Park, N.A. Huq, T.D. Foust, T. Lu, B.T. Zigler, R.L. McCormick, Towards quantitative prediction of ignition-delay-time sensitivity on fuel-to-air equivalence ratio, *Combust. Flame* 214 (2020) 103-115.
- [8] J. Cho, H.H. Song, Dimensionless parameters determining the effect of dilution on ignition delay of syngas and hydrocarbon fuels, *Combust. Flame* 213 (2020) 279-290.
- [9] M.Q. Duong, V.H. Nguyen, P.X. Pham, Development of Empirical Correlations for Ignition Delay in a Single Cylinder Engine Fueled with Diesel/Biodiesel Blends, *2019 International Conference on System Science and Engineering (ICSSE)*, 2019
- [10] S.S. Goldsborough, A chemical kinetically based ignition delay correlation for iso-octane covering a wide range of conditions including the NTC region, *Combust. Flame* 156 (2009) 1248-1262.
- [11] J. Cho, J. Luecke, M.J. Rahimi, Y. Kim, B.T. Zigler, S. Kim, Enhancing ϕ -sensitivity of ignition delay times through dilution of fuel-air mixture, *Proc. Combust. Inst.* (In press).
- [12] D. López-Pintor, J.E. Dec, Experimental Evaluation of a Gasoline-like Fuel Blend with High Renewable Content to Simultaneously Increase ϕ -Sensitivity, RON, and Octane Sensitivity, *Energy Fuels* 35 (2021) 16482-16493.
- [13] D. López-Pintor, J. Dec, G. Gentz, Experimental Evaluation of a Custom Gasoline-Like Blend Designed to Simultaneously Improve ϕ -Sensitivity, RON and Octane Sensitivity, *SAE International Journal of Advances and Current Practices in Mobility* 2 (2020) 2196-2216.
- [14] D. Kang, A. Shah, T. Rockstroh, S. Goldsborough, Utilizing Static Autoignition Measurements to Estimate Intake Air Condition Requirements for Compression Ignition in a Multi-Mode Engine-Engine and RCM Experimental Study, (2019).
- [15] A. Fridlyand, S.S. Goldsborough, M. Al Rashidi, S.M. Sarathy, M. Mehl, W.J. Pitz, Low temperature autoignition of 5-membered ring naphthenes: Effects of substitution, *Combustion and Flame* 200 (2019) 387-404.
- [16] S. Cheng, C. Saggese, D. Kang, S.S. Goldsborough, S.W. Wagnon, G. Kukkadapu, K. Zhang, M. Mehl, W.J. Pitz, Autoignition and preliminary heat release of gasoline surrogates and their blends with ethanol at engine-relevant conditions: Experiments and comprehensive kinetic modeling, *Combustion and Flame* 228 (2021) 57-77.
- [17] S. Cheng, D. Kang, A. Fridlyand, S.S. Goldsborough, C. Saggese, S. Wagnon, M.J. McNenly, M. Mehl, W.J. Pitz, D. Vuilleumier, Autoignition behavior of gasoline/ethanol blends at engine-relevant conditions, *Combustion and Flame* 216 (2020) 369-384.
- [18] S.S. Goldsborough, J. Santner, D. Kang, A. Fridlyand, T. Rockstroh, M.C. Jespersen, Heat release analysis for rapid compression machines: Challenges and opportunities, *Proceedings of the Combustion Institute* 37 (2019) 603-611.
- [19] T. Rockstroh, A. Fridlyand, S. Ciatti, W. Cannella, S.S. Goldsborough, Autoignition behavior of a full boiling-range gasoline: Observations in RCM and GCI engine environments, *Combustion and Flame* 209 (2019) 239-255.
- [20] B.W. Weber, C.-J. Sung, M.W. Renfro, On the uncertainty of temperature estimation in a rapid compression machine, *Combustion and Flame* 162 (2015) 2518-2528.
- [21] M. Mehl, K. Zhang, S. Wagnon, G. Kukkadapu, C.K. Westbrook, W.J. Pitz, Y. Zhang, H.J. Curran, M.E. Rachidi, N. Atef, A comprehensive detailed kinetic mechanism for the simulation of transportation fuels, *10th U.S. National Combustion Meeting*, 2017
- [22] D.G. Goodwin, H.K. Moffat, R.L. Speth, Cantera: An object-oriented software toolkit for chemical kinetics, thermodynamics, and transport processes, Version 2.5.1., doi:10.5281/zenodo.4527812, 2021.
- [23] M. Mehl, J.-Y. Chen, W.J. Pitz, S.M. Sarathy, C.K. Westbrook, An approach for formulating surrogates for gasoline with application toward a reduced surrogate mechanism for CFD engine modeling, *Energy Fuels* 25 (2011) 5215-5223.
- [24] W.R. Leppard, The chemical origin of fuel octane sensitivity, *SAE transact.* (1990) 862-876.
- [25] E. Singh, S.M. Sarathy, The role of intermediate-temperature heat release in octane sensitivity of fuels with matching research octane number, *Energy Fuels* 35 (2021) 4457-4477.
- [26] K.H. Yoo, A.K. Voice, A.L. Boehman, Influence of intermediate temperature heat release on autoignition reactivity of single-stage ignition fuels with varying octane sensitivity, *Proc. Combust. Inst.* 38 (2021) 5529-5538.