ESTIMATING FUEL OCTANE NUMBERS FROM HOMOGENEOUS GAS-PHASE IGNITION DELAY TIMES

NIMAL NASER^{*}, S. MANI SARATHY^{*}, SUK HO CHUNG

King Abdullah University of Science and Technology (KAUST),
Clean Combustion Research Center (CCRC), Thuwal, Saudi Arabia

^{*}Corresponding authors: nimal.naser@kaust.edu.sa; mani.sarathy@kaust.edu.sa

To cite this article:

Naser, N., Sarathy, S.M. and Chung, S.H., "Estimating fuel octane numbers from homogeneous gas-phase ignition delay times.". *Combust. Flame*, 188 (2018), pp. 307–323.

Abstract

Fuel octane numbers are directly related to the autoignition properties of fuel/air mixtures in spark ignition engines. This work presents a methodology to estimate the research and the motor octane numbers (RON and MON) from ignition delay time (IDT) data calculated at various pressures and temperatures. The hypothesis under investigation is that at specific conditions of pressure and temperature (i.e., RON-like and MON-like conditions), fuels with IDT identical to that of a primary reference fuel (PRF) have the same octane rating. To test this hypothesis, homogeneous gas-phase IDTs with a detailed gasoline surrogate chemical kinetic model have been calculated at various temperatures and pressures. From this dataset, temperatures that best represent RON and MON have been correlated at a specified pressure. Correlations for pressures in the range of 10–50 bar were obtained. The proposed correlations were validated with toluene reference fuels (TRF), toluene primary reference fuels (TPRF), ethanol reference fuels (ERF), PRFs and TPRFs with ethanol, and multi-component gasoline surrogate mixtures. The predicted RON and MON showed satisfactory accuracy against measurements obtained by the standard ASTM methods and blending rules, demonstrating that the present methodology can be a viable tool for a first approximation. The correlations were also validated against an extensive set of experimental IDT data obtained from literature with a high degree of accuracy in RON/MON prediction.

1 INTRODUCTION

One of the limiting factors in increasing thermal efficiency of spark ignition (SI) engines with higher compression ratio is autoignition characteristics of fuel related to knocking phenomenon [1]. Especially, modern SI engines with turbocharging and downsizing significantly alter in-cylinder pressure and temperature history as compared with conventional engines. In this regard, understanding fuel's chemistry and engine interactions at a fundamental level is important.

Knocking propensities of gasoline fuel have been introduced by Graham Edgar [2] in 1927 based on primary reference fuel (PRF) mixtures of *n*-heptane and *iso*-octane (2,2,4-trimethylpentane), which are paramount to oil and gas industry in fuel production. Gasoline fuels are characterized by the research octane number (RON) and the motor octane number (MON), which are specified by ASTM D2699 and D2700 [3, 4], respectively, and are measured with a Cooperative Fuel Research (CFR) engine. The engine operating condition in the RON test is with intake air temperature of 325 K and an engine speed of 600 rpm, for the MON test the intake mixture temperature, i.e., fuel-air mixture is set at 422 K and an engine speed of 900 rpm and the knocking behavior is compared with that of PRF. Based on the test method, the volume percentage of *iso*-octane in the matching PRF mixture represents the RON or the MON of the fuel. The higher operating temperatures in the MON test and the absence of negative temperature coefficient (NTC) [5, 6] behavior in practical automotive fuels lead to the knock characteristics in a MON test to match a PRF lower than that it matched at the RON test due to strong NTC behavior exhibited by PRFs [7].

To extend the effects of engine operating conditions on anti-knock quality of fuels, Kalghatgi [8, 9] proposed the octane index (OI), an engine-fuel metric that considers the autoignition quality of a fuel at different engine operating conditions, which is defined as

$$OI = (1 - k)RON + kMON \quad (1a)$$

$$OI = RON - kS \quad (1b)$$

where k is a constant representing an engine operating condition and S is the octane sensitivity defined as $RON - MON$. Thus, $k = 0$ (1) corresponds to RON (MON) condition. It has been shown that the k factor is shifting towards negative values in modern SI engines with downsizing and turbocharging, implying that they are operating away from RON/MON range [10].

Numerous efforts have been performed to advance fundamental understanding of the relationship between octane number and fuel chemistry. The earliest attempt in understanding the effect of molecular structure on fuel's antiknock quality was done by Lovell and co-workers [11, 12, 13, 14, 15], wherein they studied the knock characteristics of 27 paraffins [11], 25 aliphatic olefins [11], 69 naphthenes [13] and 22 aromatics [14] using aniline as a standard for rating fuels. They were able to establish a consistent

connection with molecular structure and knock propensity. Lovell’s work paved the way for a systematic approach in comprehending engine knock from a chemical kinetic perspective followed by Downs et al. [16, 17], Pahnke et al. [18], Walcutt et al. [19], Walsh [20], and Westbrook et al. [21].

Studies linking molecular structure and chemical kinetics were closely followed by determining RON and MON from chemical composition [22, 23, 24, 25, 26] as gasoline is composed of many hydrocarbons [27], whose compositions are subject to great variability [28]. This complex compositional variability has initiated the need for surrogate fuels that can accurately predict specified target properties depending on the application. Morgan et al. [29] developed nonlinear blending rules for ternary surrogates composed of toluene, *iso*-octane and *n*-heptane, termed toluene primary reference fuels (TPRF). Empirical correlations between TPRF surrogates and RON/MON were developed by Kalghatgi et al. [30] where RON/MON of TPRF surrogates were obtained with standard ASTM tests [3, 4]. There remains a continued interest in determining RON and MON values of gasoline fuels using surrogate mixtures; this study correlates simulated ignition delay times (IDT) of various surrogate mixtures with their RON and MON values. The RON and the MON used for developing the correlations were determined via blending rules [30, 31], experimental RON/MON measurements done at Saudi Aramco’s Research and Development Center (R&DC) [32] and in many cases obtained from literatures [33, 30, 34, 31].

IDT is an important target property in surrogate fuel formulation, among many others, including chemical composition, H/C ratio, RON/MON/AKI (antiknock index, $AKI = \frac{RON+MON}{2}$) [35, 36, 37, 38], density, and distillation characteristics [39, 40, 41, 42]. Insights into the chemical aspects of octane sensitivity ($S = RON - MON$) were reported by Leppard [7], attributing octane sensitivity to the NTC behavior of paraffinic PRF mixtures whose autoignition chemistries are different from those of aromatics, olefins, and cycloalkanes found in gasoline. Recently, Westbrook et al. [43] attributed the octane sensitivity of various fuels (e.g., alcohols, olefins, aromatics, etc.) to the effects of electron delocalization on low temperature reactivity. Griffiths et al. [44] attempted to correlate IDT with octane rating, but were unable to find suitable correlations between them, instead they proposed that minimum autoignition temperature could lead to better correlation between octane numbers.

Mehl et al. [35] correlated the slope of IDT curves in Arrhenius plots with octane sensitivity of the fuel. A higher slope in NTC regime corresponded to higher sensitivity of the fuel. They were also able to correlate AKI to IDT at an initial pressure of $P_0 = 25$ atm and initial temperature $T_0 = 825$ K. Sarathy et al. [45] proposed IDT measurements at 20 atm and 835 K could be correlated with RON. The proposed correlations were validated with isomers of octane and it was observed that the predicted RON was in close agreement with measured RON. Ahmed et al. [40] further validated these conditions with gasoline surrogates. Badra et al. [46] reported relationships between RON and MON and simulated IDT of PRF, toluene/*n*-heptane mixtures (toluene reference

fuel, TRF) and TPRF. In their work, pressure and temperature conditions providing suitable relationships between octane rating and IDT were identified and correlations for those conditions were reported. Four conditions were identified in [46] where RON and MON could be correlated with IDT, for RON predictions, simulated IDTs at 50 atm and 850 K provided the best fit. For MON predictions in [46], variable volume profiles, wherein the cylinder volume profile during standard MON tests in CFR engine along with their pressure and temperature histories, served as input for IDT calculations, that were subsequently used in estimating MON.

Most studies have put forward correlations of ON/sensitivity with IDT at one specific condition of pressure and temperature, and in most cases the conditions where RON and MON are correlated have different pressure. While the present work attempts correlations at multiple pressures, and in addition the RON-like and MON-like temperature for each pressure are also given. This could be of particular use to experimentalists employing shock tubes (ST) and rapid compression machines (RCM), to measure IDT at one particular pressure, due to changes in the experimental configuration/settings. To the authors' best knowledge, this is also the first attempt in linking IDT (obtained from simulations) to OI in homogeneous reactors; Bradley and Head followed a similar approach [47] that relies on OI obtained from engine experiments. Although OI is not an intrinsic fuel property, it is a measure of the autoignition resistance of a fuel at a specified condition. The OI is a combination of physical operating conditions taken into account by the " k " factor and the chemical characteristics taken into account by the fuel's autoignition quality, RON and MON. Correlations between IDT and OI at conditions "beyond RON", where modern SI engines operate, are also provided. The " k " factor are determined experimentally with engine tests, and in such cases are subject to uncertainties. However, in our studies the conditions at which " k " achieves certain values (i.e., $k = 0.5, -0.5, -1.0$) are identified. The " k " value conditions presented in this work may not exactly match to " k " value conditions measured in an engine, but the approach is applicable in assessing the autoignition resistance of fuels in STs and RCMs at conditions relevant to modern SI engines.

Recently, Naser et al. [48] measured IDTs (referred to as IDT_{IQT}) using an ignition quality tester (IQT) for gasolines and their surrogates, which have relatively long IDT_{IQT} as compared to diesel fuels such that the contribution of physical delay times (such as spray evaporative cooling and mixing) are relatively short, thus the IDT_{IQT} can be reasonably related to chemical delay time. A methodology has been developed to correlate RON and MON of gasoline-like fuels to IDT_{IQT} data. This work clearly implies that simulated IDT and IDT measured in STs and RCMs can be correlated to knocking propensities of gasoline fuels. The methodology in [48] related the IDT_{IQT} of a non-PRF to that of a PRF at a fixed pressure and equivalence ratio and multiple temperatures. The difference in IDT_{IQT} of the non-PRF compared to PRFs were related to the RON and MON of the test fuel. A fuel that has an IDT_{IQT} matching that of PRF X at multiple temperatures has zero sensitivity, so will behave like PRF X at both

RON and MON conditions. On the other hand, a fuel that has an IDT_{IQT} matching that of PRF X at one temperature and an IDT_{IQT} matching that of PRF Y at another temperature has octane sensitivity, more details are available in [48].

Chemical kinetic models have expanded to model large molecules up to C_{20} *n*- and *iso*-alkanes [49], and keep on expanding to include molecules covering many gasoline hydrocarbon classes. Nevertheless, detailed chemical kinetic models still often fail to predict ignition behavior of practical fuels, when tested across a wide range of temperature and pressure conditions [42]; which could either be due to errors in the choice of surrogates, the chemical kinetic model itself, or a combination of both. One among many target properties in surrogate fuel formulation is ON, the RON/MON of the surrogate fuel is estimated with blending rules available in literature [35, 40]. Motivated by our previous work [48], the present work attempts to correlate IDTs calculated from a detailed kinetic mechanism to knock propensities of gasoline fuels to develop an ON estimation tool. The correlations developed could be considered an additional target property in surrogate fuel formulation, since surrogate performances are evaluated in IDT space [40], this could lead to better surrogate fuel formulations. PRF, TRF and TPRF fuels are used to establish a methodology that has been extended to ethanol mixtures to validate the methodology. The methodology has been extended to existing measured IDTs from ST and RCM to test the predictive capability from such canonical experiments in estimating knock propensity.

Many researchers [50, 51, 52, 53, 54, 55] have suggested that the octane numbers be replaced with a better fuel metric for antiknock quality. However, octane numbers are ubiquitous in the oil and gas industry. Replacing these metrics requires aggressive fuel policies, which is a challenging effort because refinery operations have become accustomed and calibrated to these important, yet old fuel metrics. Such a move could be easily avoided if the existing fuel metrics could be used to infer fuel behavior in modern engines; this was Kalghatgi's idea of octane index [8, 9], wherein a physical parameter was introduced to represent a real engine's operating conditions with respect to the CFR engine's RON and MON conditions. The intention with the present work is not to replace the standard methods ASTM D2699 and D2700 [3, 4] for RON and MON, but instead as an initial screening tool to estimate a fuel mixture's RON and MON. This approach helps isolate the autoignition chemistry from the competing effects of charge cooling, residual gases, equivalence ratio variations (0.9–1.1), and flame speed, which may affect knocking tendency. The difference in flame speed affects the unburned gas pressure- temperature history, but it is also observed that for most high carbon number hydrocarbons the laminar flame speeds are reasonably similar. There are differences in flame speed due to turbulence, but it is the autoignition chemistry of the end gas that plays the major role in defining the knock characteristics [1]. Residual NO remaining in the cylinder after exhaust valve closure has an influence on the flame speed and ignition chemistry, as shown in a recent study by Foong et al. [56]. These factors play

an important role in predicting knock onset with chemical kinetic models coupled with computational fluid dynamics.

The objective of our work is to correlate the ignition characteristics in a complex CFR engine environment with an ideal chemical kinetic metric, specifically the homogeneous gas-phase ignition delay time. One of the reasons this study correlates homogeneous gas-phase IDT with RON and MON is because the former is a fundamental kinetic parameter and goes beyond any industry accepted measurement. By linking a practical metric, such as RON/MON, to the fundamental IDT, the present work demonstrates that the widely accepted metric could be replaced by parameter that is intrinsically less uncertain and also more relatable to various engine configurations and operating conditions.

Our approach is focused on the chemical aspect of knock neglecting physical effects. This could help provide better chemical kinetic insights for fuel design of higher antiknock quality of fuels. When designing fuel formations, it is important to have reasonable estimates of the mixture's RON and MON. For ASTM D2699 and D2700 [3, 4], sufficient amount of fuel is required to measure RON and MON, and the testing can become time consuming and expensive. Furthermore, blending rules for many hydrocarbon components and oxygenates may not be readily available or are not well validated. The correlations proposed herein allow estimation of a fuel mixture's RON and MON from simulated IDT, or with as little as, say 250 mL of fuel by conducting IDT measurements in ST and RCM at specific conditions. Finally, the operating conditions of modern SI engines have shifted from the standard RON and MON tests. Although these tests are still followed in oil refineries worldwide to benchmark automotive fuels, this paper identifies the conditions in ST and RCM that are relevant to modern SI engines, which is essential to design fuels for future engines.

2 METHODOLOGY

End gas autoignition results from a cumulative effect of a specific pressure-temperature trajectory and compression due to the advancing flame front. The overall process is recognized as being extremely complex. Both chemical kinetic and physical properties play an important role in predicting knock onset with chemical kinetic models and computational fluid dynamics. Our approach is focused on the chemical aspect of knock and neglects the physical effects. By doing so, the aim is to provide better chemical kinetic insights for fuel design of higher antiknock quality of fuels. The methodology presented in this paper is based on the assumption that at specific conditions of pressure and temperature, the IDT of gasoline fuel and its RON/MON are correlated.

This study is not the first one approximating the cumulative effects of ignition characteristics along a specific pressure-temperature trajectory by examining ignition delay at one condition, in fact many studies are based on this approximation [35, 45, 46, 32]. Note that RON and MON tests represent specified initial temperature and engine

speed conditions, which in turn alter the end gas temperature and pressure conditions where autoignition occur ahead of spark-initiated flame front to reach. To account for varying engine operating condition and its effects on end gas, Kalghatgi et al. [57] proposed T_{comp15} as a representative of unburned bulk gas temperature at specified pressure of 15 bar. This work identifies a specific temperature for a given pressure at which RON and MON are correlated with IDT, which are designated as “RON-like” and “MON-like” temperatures. The correlations are then used to predict RON and MON of various fuels mixtures.

The basic premise is that any fuel mixture having the same IDT as that of a PRF mixture (at the same conditions) should have the same octane number as the PRF. Thus, at RON-like (or MON-like) conditions, the ON of a fuel relates to the RON (or the MON) values of corresponding PRF. It is possible that fuels with different RON/MON values have the same IDT particularly at very high temperatures ($T_0 > 1000$ K) [42, 58] and very low temperatures ($T_0 < 700$ K) for low RON fuels [58]. However, in the temperature regime corresponding to the NTC region, IDT has strong dependence on ONs as indicated by many studies [59, 35, 58], which has motivated the present work to investigate IDTs in the NTC region.

All fuel mixtures used here are available in the Supplementary Material (SM) listed in Tables S1 to S7. Table S1 lists the composition of PRF mixtures that are used in developing correlations between ON and IDT. Tables S2 and S3 list the compositions of TRFs and TPRFs, respectively. The RON and the MON for TRF and TPRF mixtures were determined according to the blending rule proposed by Kalghatgi et al. [30], which is based on a set of extensive experimental engine data. This blending rule was able to predict the RON and MON of TPRFs available in literature extremely well indicated by high correlation coefficients R^2 of 0.9998/0.9976 for RON/MON, respectively, reported in [30]. Although, the effectiveness of this rule can be quantifiably assessed against real measured data, due to limitations of extensive RON/MON measurements of TRF and TPRF, the TPRF blending rule [30] is used here. Tables S4 and S5 list the compositions of ethanol reference fuels (ERFs; binary mixtures of ethanol and *n*-heptane) and ethanol primary reference fuels (EPRFs; ternary mixtures of ethanol and PRFs), respectively. Table S6 lists the composition of ethanol toluene primary reference fuels (ETPRFs; quaternary mixtures of ethanol and TPRFs). Several measured RON and MON for ethanol mixtures were available, however for certain mixtures the limited data required RON/MON to be determined with the blending rule from AlRamadan et al. [31]. This blending rule was demonstrated to be applicable for a wide range of ON for PRFs and TPRFs mixed with ethanol. Table S7 lists the compositions of various multi- component surrogate blends (MCSB) comprising *n*-heptane, *iso*-octane, toluene, 1-hexene, and 1,2,4-trimethylbenzene (124-TMB), and cyclopentane (CPT) whose RON and MON were determined with standard test methods prescribed by ASTM D2699 [3] and ASTM D2700 [4], respectively, at Saudi Aramco [32].

The following naming convention is used throughout this paper, PRF X: X vol.% of *iso*-octane and remaining *n*-heptane, TRF X: X vol.% of toluene and remaining *n*-heptane and for TPRF X-Y: X vol.% of toluene, Y vol.% of *iso*-octane and remaining *n*-heptane. ERF and EPRF follow the same naming convention as those of TRF and TPRF with ethanol replacing toluene, while for ETPRF X-Y-Z: X indicates vol.% of ethanol, Y vol.% of toluene, Z vol.% of *iso*-octane and remaining *n*-heptane. No naming convention is followed for MCSBs and they are identified by their blend numbers in Table S7.

Homogeneous gas-phase IDTs of all mixtures were simulated using a batch reactor code in Cantera [60] with the KAUST-LLNL-NUIG gasoline surrogate chemical kinetic model [42] that has been validated against ST and RCM as reported in [42]. All IDTs were calculated at stoichiometric conditions ($\phi = 1$) with pressures in the range 10–50 bar at 5 bar intervals. For each pressure, IDT at 10 K interval in the initial temperature range of $T_0 = 700$ –1000 K were calculated. IDT was defined as the time interval from the initial reactor temperature to a reactor temperature 400 K above the initial temperature. This criteria for ignition yields similar values as using the maximum change in temperature versus time ($\max dT/dt$), and is commonly used in chemical kinetic studies [38, 42, 45]. The correlations presented later are developed using simulated IDTs; however, as shown later, experimental IDT values have also been utilized to further test the applicability of the methodology.

2.1 RON-like and MON-like conditions

The proposed methodology can best be explained by presenting an example at a specified pressure of 20 bar. Figure 1 shows IDTs of various PRFs calculated with the KAUST-LLNL-NUIG gasoline surrogate chemical kinetic model [42] along with IDTs of several TRFs. The IDTs of PRFs clearly show the characteristic NTC behavior, i.e., increasing IDT with increasing temperature in the range of initial temperature $T_0 = 800$ –900 K. This PRF data serves as baseline data in our methodology.

Figure 1: Simulated IDTs of various PRFs (gray lines) and TRFs and TPRFs (colored lines) at $P_0 = 20$ bar. Temperatures corresponding to RON-like, MON-like, and AKI-like conditions are denoted by the dotted lines.

Various correlations between octane numbers and calculated IDTs have been proposed for specific temperature and pressure conditions in [35, 46, 45]. Motivated by the methodology used in our previous work on relating octane number with IDT_{IQT} , i.e., τ_{id} in IQT experiments [48], a relation of the following form is sought in relating ON and τ_{id} [ms].

$$ON = a \times \tau_{id}^n + b \quad (2)$$

where a , b , and n are the coefficients and exponent, respectively, at specified temperature and pressure. This equation relates ON as a linear function of τ_{id}^n . Note that for PRFs, octane numbers are prescribed by definition (say at RON and MON conditions from ASTM D2699 and D2700 [3, 4]). Proceeding in a similar manner, the IDT of PRF (i.e., simulated τ_{id}) is fit by Eq. (2) using an ordinary least squares method for each temperature in the range of 700–1000 K. As 31 different temperature points are available in this range at 10 K intervals, 31 sets of coefficients and exponent (i.e., a , b , and n) were obtained for one particular pressure.

The coefficients and exponents vary across the entire temperature and pressure range, as IDT of PRFs varies with temperature and pressure. Using simulated IDT of non-PRFs, i.e., TRFs and TPRFs these 31 sets of coefficients and exponent are then tested at one particular pressure. IDT of a non-PRF at one specific temperature with

constants at the same temperature and pressure were used in estimating the ON. At a given pressure, two specific temperatures were identified, such that the estimated ONs best matched the available RON and MON. These temperatures are identified as the RON-like and MON-like temperatures for a given pressure. The steps are repeated for other pressures to identify the RON-like and MON-like temperature at the respective pressures. Note that these temperatures are not the end gas temperatures observed in an SI engine rather conditions in a homogeneous reactor such as ST or RCM where IDT and RON/MON are correlated.

The present methodology identifies temperature and pressure conditions at which ON can be predicted based on IDT obtained from chemical kinetic simulations; for example, the variation of ON with IDT at 20 bar is shown in Fig. 2. The black curves in Fig. 2 depict correlations that were generated with IDT of PRF at 20 bar for RON-like and MON-like conditions using Eq. (2). These figures are shown only to provide a qualitative idea on the variation of ON with IDT. The variations of IDT with RON and MON at other pressures are shown in Figs. S1 and S2.

Figure 2: Variation of RON and MON with IDT at 20 bar of PRFs, TRFs and TPRFs. Solid lines indicate correlations obtained with IDT of PRF, in the functional form given by Eq. (2).

As an example, the IDT of TRF 50 at $P_0 = 20$ bar and $T_0 = 720$ K, is 5.44 ms. At the condition, the constants a , b , and n are -420.47 , 111.94 and -1.35 , respectively. Substituting the IDT and the constants in Eq. (2), the predicted ON is 69.2 as compared with the measured RON of 65.1. The IDT of TRF 50 at other temperatures, corresponding constants were used in estimating ON. Among these data set, the best fit temperature for RON estimation can be found. The same steps were followed to identify the temperature that best predicted MON. Applying these steps to all the non-PRFs, the RON-like (MON-like) temperature T_{RON} (T_{MON}) that can best represent nominal RON (MON) for TRF and TPRF fuels determined from either standard ASTM tests or using blending rule [30] has been found to be $T_{RON} = 750$ K and $T_{MON} = 820$ K as marked in Fig. 1.

Figure 1 also shows that the IDT data of TRFs and TPRFs intersects the IDTs of PRFs. Take for example TRF 75, for which the IDT at 20 bar and 750 K intersects with the IDT of PRF 97, and at 820 K intersects with the IDT of PRF 87. This implies that for a specified pressure, octane number varies with temperature. Now one can select RON-like and MON-like temperatures such that determined octane numbers from the calculations best match nominal RON and MON values of test fuels (TRF in this case). For example, if one selects RON (MON)-like temperature as 750 (820) K, the estimated RON/MON of TRF 75 is 97/87, respectively, which is close to the nominal RON/MON of TRF 75 being 94/83, respectively. For the specified TRF fuel, the IDT intersects with that of a lower octane PRF as the temperature increases (i.e., MON is lower than RON).

As an another example, consider the IDT of TPRF 30-55 at 20 bar in Fig. 1(b). At the RON-like temperature of 750 K (refer to Table 1), TPRF 30-55 and PRF 92 have the same IDT. This suggests that TPRF 30-55 has a RON of 92. The nominal RON for this mixture determined using empirical correlations in [30] is 91. At the MON-like temperature of 820 K, TPRF 30-55 and PRF 87 have similar IDT, thereby providing a MON prediction of 87. Empirical correlation in [30] provide a MON 86 for TPRF 30-55. It can be observed that an increase in octane sensitivity (larger difference between RON and MON) with increasing toluene percentages in the TPRF mixture. These observations are consistent with Leppard’s explanation [7] on the origins of octane sensitivity of gasolines. Note that the MON-like condition is observed in the NTC regime of PRFs, consistent with the findings of Leppard [7].

3 RESULTS AND DISCUSSION

This section presents details on the selection of RON-like and MON-like conditions, the use of correlations to estimate RON and MON from simulated IDT, and verification of the approach using various chemical kinetic models. Validations at conditions typical to modern IC engines known as “beyond RON” conditions are also presented.

Figure 3: Predicted and nominal (a) RON and (b) MON of PRF, TRF and TPRF with IDT calculated using the KAUST-LLNL-NUIG gasoline surrogate model [42] at $P_0 = 20$ bar

Figure 3 shows predicted RON and MON at 20 bar for PRF, TRF and TPRF mixtures with a , b and n as $-179.68, 106.60$ and -1.11 for RON and $-101.85, 98.45$ and -0.87 for MON, respectively. As mentioned above for 20 bar, the IDTs for RON and MON predictions are to be evaluated at 750 K and 820 K, respectively. The predictions at other pressures will be discussed later. The predicted values are in satisfactory agreement with nominal values as indicated by the small root mean square error (RMSE) of 3.7 and 2.5 for RON and MON, respectively. The absolute error in the predictions of RON and MON with IDT at 20 bar along with the ASTM RON and MON repeatability and reproducibility limits are shown in Fig. S3. The average errors in the predictions of RON for PRF/TRF/TPRF are 2.7/4.4/3.0, respectively, and for the MON predictions are 3.0/2.5/1.7. Note, the agreement deteriorates for the TRF fuels for RON and MON values higher than say 100, which can be partially understood since the scales for PRFs are between 0 and 100, such that extrapolations are required. In spite of the above shortcomings, the correlations are able to predict RON and MON with substantial degree of accuracy indicated by the high $R^2 > 0.981/0.990$ and $RMSE < 3.7/2.5$ for RON and MON, respectively.

The sources for these errors are multiple, including errors associated with RON/MON measurements as discussed in the ASTM standards [3, 4]. Mixing of

primary reference fuels and other surrogate fuels could also be subject to errors which are difficult to quantify. The most important source of error is the discrepancy in chemical kinetic models in accurately simulating IDTs of hydrocarbon fuels. However, the present methodology works with widely varying chemical kinetic models developed by different groups. By calibrating the model with PRF IDT simulations, this approach cancels many errors associated within the kinetic models for predicting IDT of an unknown fuel. A thorough quantification of all sources of error in every measurement and correlation is beyond the scope of the present work and not discussed hereafter.

Comparison of the estimated and nominal RON/MON values of PRFs, TRFs, and TPRFs with simulated IDT obtained from other kinetic models was also assessed, and are given in the Supplementary Material. Three other models were selected and utilized in the present study, specifically: (i) LLNL detailed gasoline surrogate model [61], (ii) RWTH optimized gasoline surrogate model [62], and (iii) POLIMI PRF surrogate model [63]. As discussed in the Supplementary Material, RON and MON predicted using simulated IDT with different chemical kinetic models show close agreement with nominal values, with some deviations primarily in lower octane number range.

The previous comparisons demonstrate the validity and broad applicability of the present RON and MON prediction methodology. The coefficients determined in Eq. (2) are useful in estimating RON and MON of fuels whose IDT are experimentally measured at RON-like and MON-like conditions (experimental validations provided later) or calculated with another chemical kinetic model (given in Supplementary Material). As the methodology is able to predict RON and MON of PRF, TRF and TPRF with sufficient degree of accuracy, it was next extended to mixtures containing ethanol and multicomponent gasoline surrogates.

3.1 *Validation with other mixtures*

In this section, RON and MON predictions for mixtures containing ethanol (ERF/EPRE/ETPRF), and multicomponent surrogate blends are discussed. Nominal RON and MON values for ERF, EPRE, and ETPRF mixtures were obtained from [34, 64, 31]. The IDT of all mixtures in [34, 31] were calculated using the KAUST-LLNL-NUIG gasoline surrogate model [42]. Predicted RON and MON of different mixtures are shown in Fig. 4 for IDT calculated at 20 bar with the same conditions, coefficients and exponent used for the previous TRF and TPRF predictions.

Figure 4(a) and (b) shows predictions of mixtures containing ethanol. Small errors for RON and MON can be observed at 20 bar, as indicated by $R^2 = 0.975/0.952$, $RMSE = 3.2/3.7$ for RON and MON, respectively, demonstrating the accuracy of correlations in predicting RON and MON with simulated IDT.

Figure 4: Predicted and nominal RON (left) and MON (right) of ethanol mixtures (top), multicomponent surrogates (bottom), IDT calculated using the KAUST-LLNL-NUIG gasoline surrogate model [42] at $P_0 = 20$ bar

For fuels with high ethanol content, charge cooling due to ethanol's high latent heat of vaporization (HoV) increases the mixture's RON as discussed in Foong et al. [65]; this is one of many studies [66, 67, 68] that attributes increased knock resistance of ethanol and gasoline-ethanol blends to higher HoV of ethanol. The standard RON test [3] prescribes the temperature of air upstream of the carburetor to be 323 K, so fuels with high HoV cool the charge by evaporative cooling. This decreases in-cylinder temperature compared to a PRF and enhances the octane rating of such high HoV fuels. A recent study attributes the HoV effect as a thermal contributor to octane sensitivity [69]. Studies in [69] indicate that for fuels with fixed octane sensitivity and varying HoV, the anti-knock quality of fuels correlated with the fuels' RON, and HoV provided no additional benefit [69]. Our predictions of RON of mixtures containing ethanol are with fully homogeneous gas-phase IDTs, and no charge cooling effects are considered. It should be noted that the MON test [4] prescribes temperature downstream of the carburetor, so that the charge cooling effect of ethanol does not play a role in the octane test.

The model was also tested by simulating IDT of MCSBs (at 20 bar, 750 and 820 K) and then predicting their RON and MON. The mixtures comprised *n*-heptane, *iso*-octane, toluene, 1-hexene, 1,2,4-trimethylbenzene, and cyclopentane (CPT) and their RON and MON were measured in [32] by standard ASTM methods D2699 and D2700 [3, 4]. Nominal RON and MON values are given in Table S7. Comparison between predicted

and nominal RON and MON are shown in Figs. 4(c) and (d) for MCSBs, respectively, for IDT calculated at 20 bar. Although predictions are somewhat poor compared to other mixtures ($R^2 = 0.898/0.910$, $RMSE = 3.0/2.7$ for RON and MON, respectively), the correlations are able to estimate the approximate range of ON, which is helpful for initial surrogate fuel screening procedures.

3.2 Pressure effect

The methodology was subsequently tested with simulated IDT for all the above mixtures at other pressure conditions. As discussed in the methodology section, the RON-like and MON-like temperatures identified at each pressure condition is given in Table 1, and plotted in Fig. 5, marked as $k = 0$ and 1 , respectively for RON and MON. The MON-like temperatures at each pressure were higher than RON-like temperatures; this was consistent with the standard MON and RON tests [3, 4], wherein the MON test has higher intake mixture temperature and engine speed, thus higher end-gas temperatures. Table 1 lists the exponent, n , and the coefficients a and b that correspond to each pressure and temperature condition. The temperatures shown in Fig. 5 denote the temperatures at which IDT of any unknown mixture should be determined and then substituted in Eq. (2) for RON/MON with corresponding exponent and coefficients given in Table 1 to determine the mixture's RON/MON. Figure 5 also shows pressure and temperature conditions for k values other than 0 and 1 that will be explained later in this section. The variation of the exponent and coefficient with pressure is given in Fig. S4 in Supplementary Material.

Table 1: Exponent n and coefficients a, b in Eq. ((2)) to predict RON and MON

P_0 [bar]	RON				MON			
	T_0 [K]	n	a	b	T_0 [K]	n	a	b
10	730	-0.99	-296.01	106.11	780	-0.85	-206.26	97.68
15	740	-1.04	-234.57	106.60	800	-0.88	-138.00	97.83
20	750	-1.11	-179.68	106.62	820	-0.87	-101.85	98.45
25	760	-1.19	-132.07	106.10	840	-0.88	-85.05	99.32
30	770	-1.23	-95.91	105.58	860	-0.90	-74.92	100.29
35	780	-1.21	-73.28	105.64	880	-0.93	-67.81	101.47
40	790	-1.14	-61.85	106.59	900	-0.98	-61.22	102.59
45	810	-1.07	-56.32	108.05	920	-1.10	-53.35	103.15
50	820	-1.02	-51.65	109.45	940	-1.29	-43.19	103.10

Figure 5: Simulated RON-like and MON-like temperature conditions for various pressures

Figure 5 shows the possible values of k , a linear weighting factor given in Eq. (1). Note that k is a factor that depends entirely on physical conditions (temperature and pressure) in an SI engine [57] and takes into account how far the condition is from the actual RON and MON test conditions. By definition, $k = 0$ in the RON test and $k = 1$ in the MON test. Lines denoting a range of k values from IDT simulations of PRF are shown in Fig. 5 that were determined by linear interpolation and extrapolation as k is observed to be linear with T_{comp15} for two temperature ranges [57] as given by Eq. (3). Since the domain of interest is $k < 0$ which has $T_{comp15} < 825$ K and was linear, the extrapolations were also carried out linearly.

Recently Szybist and Splitter's [70] study showed that the relation given by Eq. (3) was not universally applicable. They proposed a new relation based on comparison of CA₅₀ variation at knock limited spark advance (KLSA) conditions in SI engines. The use of CA₅₀ to rate knock characteristics of fuels and thereby OI may yield different results than the method used by Kalghatgi [8, 57] where spark timing was used. The difference in methods were also explicitly stated by Szybist and Splitter [70].

Inspite of these differences a linear relation was obtained in Szybist and Splitter's study [70], and in the present work relations obtained in [57] are used. It is to be noted this temperature is the unburned bulk temperature observed in engine experiments and not the homogeneous reactor temperature.

$$k = \begin{cases} 0.0056T_{comp15} - 4.68 & \forall T_{comp15} < 825 \text{ K} \\ 0.0426T_{comp15} - 35.20 & \forall T_{comp15} > 825 \text{ K} \end{cases} \quad (3a)$$

$$(3b)$$

More details on k and its physical significance are available in [10, 71, 72]. Values of pressure and temperature at k values other than 0 and 1 are also shown in the figure. The interpretation of k values can be understood with an example. The IDT at 20 bar and 785 K relates to the antiknock index (AKI), defined as (RON+MON)/2 as this condition corresponds to $k = 0.5$. The "AKI-like" temperature at pressure 20 bar is shown in Fig. 1(b) at which IDTs of TPRF 30-55 and PRF 89 are the same, providing an AKI value of 89. In modern SI engines, the value of k can be negative [10, 71, 72], so IDT measurements of fuels at conditions in the blue shaded region in Fig. 5 are of interest for future advanced SI engines.

Comparisons of RON/MON predictions with the above mixtures at pressures from 25–40 bar are shown in Figs. 6 to 8, predictions at other pressures are available in Figs. S7 to S9 in SM. The estimated RON/MON of PRFs, TRFs and TPRFs using the KAUST-LLNL-NUIG detailed gasoline surrogate model is shown in Figs. 6(a) and 6(b). As indicated by the R^2 and RMSE, the predictions had great degree of accuracy, with the highest RMSE (least accurate) of 6.3 and 4.3 for RON and MON, respectively, observed at 50 bar. Predictions of RON and MON of ethanol containing mixtures are given in Figs. 7(a) and 7(b), respectively. The predictions show sufficient degree of accuracy indicated by the high R^2 and small values of RMSE, the least R^2 and highest RMSE is 0.859 and 6.5 for MON predictions at 40 bar. The error in predictions of RON and MON are give in Figs. S5 and S6.

The RON and MON of multicomponent surrogates are also predicted at different pressures giving reasonable accuracy in estimations, comparisons are shown in Figs. 8(a) and 8(b). The R^2 and RMSE are in the range of 0.783–0.886 and 4.5–3.1. The prediction capabilities are lesser than the reproducibility and repeatability limits of ASTM tests. As mentioned above, ASTM tests are time consuming and expensive, such that composition based correlations could be used to estimate RON and MON for a complex mixture for initial screening. However, such correlations are not always accurate, especially when dealing with mixture containing ethanol. Even the well-regarded model by

Ghosh et al. [26] has difficulties to apply because non-linear interaction parameters are not provided for all the compositional variations that one encounters in real surrogate fuel formulation (i.e., some of interaction parameters have been kept confidential). The present approach also provides a way of estimating RON and MON for a mixture of hydrocarbons where no ASTM measurement has been taken. This could be achieved by either simulating IDT or performing a ST or RCM experiment.

With correlations for multiple pressures, it was imperative to test the accuracy of the correlations with pressure. To this end, the R^2 and RMSE of all the mixtures tested in the present work at various pressures are shown in Figs. S11 and S12, respectively. When all fuels are considered the most accurate predictions for RON and MON were obtained at 20 bar. This is expected as most experiments for validation of chemical kinetic models are carried out close to 20 bar, improving the accuracy of the models at 20 bar. The higher accuracy of the correlations at 20 bar makes it practically convenient for experiments involving STs and RCMs that are typically done at 20 bar. Amongst all the fuels tested, the least accurate correlations were obtained for 50 bar, this could be possibly due to the scarcity of data at high pressures to validate chemical kinetic model.

(a)

(b)

Figure 6: Predicted and nominal (a) RON and (b) MON of PRF, TRF and TPRF with IDT calculated using the KAUST-LLNL-NUIG gasoline surrogate model [42] at different pressures

(a)

(b)

Figure 7: Predicted and nominal (a) RON and (b) MON of ERF, EPRF and ETPRF with IDT calculated using the KAUST-LLNL- NUIG gasoline surrogate model [42] at different pressures

(a)

(b)

Figure 8: Predicted and nominal (a) RON and (b) MON of MCSB with IDT calculated using the KAUST-LLNL-NUIG gasoline surrogate model [42] at different pressures

3.3 Validation with experimentally measured IDT

The present methodology has been shown to be applicable for a range of mixtures wherein the IDT is simulated using a chemical kinetic model. However, the methodology could be equally valuable in predicting the RON and MON of mixtures for which only experimental measurements of homogeneous gas-phase IDT are available. A prediction methodology based on experimental measurements could be valuable in situations wherein detailed chemical kinetic models do not exist or when real gasoline fuel mixtures are studied and simulating their IDT requires complex surrogate mixtures. It is to be noted that STs and RCMs have non-idealities [73, 74, 75] associated with IDT measurements particularly for fuels with longer IDT [75, 76]. Bradley et al. [77] investigated the differences in IDT of stoichiometric *iso*-octane in 7 different RCMs available worldwide; observing differences in IDTs at low and intermediate temperatures. The differences in measured IDT were attributed to three possible causes as discussed in [77]: (i) heat loss after the end of compression (ii) reactions that could occur during compression (iii) rebound of the piston and non-uniform ignition. More details on uncertainties and issues with RCM operation are available in [76].

To this end, the correlations in Eq. (2) obtained using simulated IDT are validated against an extensive set of experimental IDTs obtained from literature. IDTs obtained from STs and RCMs are used for validation; all IDTs used in the present study are given in Table 2 along with the facility used and their references. Some measurements employ RCM for low temperature measurements and ST for high temperature measurements and are indicated in Table 2 as ST (HT). In some cases, the IDT required to predict RON/MON at the respective measurement pressures were not available, so the IDT was obtained by linear interpolation as indicated in Table 2. Experimental IDT measurements at pressures other than those used in the present study were also observed in certain cases, so the exponent n and coefficients a and b were obtained by linear interpolation as indicated in Table 2; the linear interpolation of the exponent n and coefficients a and b are shown in Fig. S4 in Supplementary Material.

Comparisons between predicted and nominal RON/MON are given in Fig. 9. The correlations obtained are able to predict RON/MON with great degree of confidence, particularly in the higher ON range. It is to be noted that the ON measurements by ASTM standards [3, 4] utilize a digital counter setting for RON/MON greater than 40. Per the standard, RON/MON measurements are acceptable only above ON 40, and in spite of this, the RON/MON measurements of pure components below 40 were reasonably well predicted as shown in Table 2. The error in predictions of RON and MON with experimentally obtained IDT is shown in Fig. S10.

Table 2: Predicted RON and MON with experimental IDT

S. No.	Fuel	P_0 (bar)	$\tau_{id,RON}$ (ms)	$\tau_{id,MON}$ (ms)	Device	τ_{id} Ref.	Predicted		Nominal		RON/MON Ref.
							RON	MON	RON	MON	
1	Propane	30 ¹	40.21	38.84	RCM	[83]	104.6	97.5	109.4	96.3	[84]
2	<i>n</i> -butane	15	13.73 ²	15.18	RCM	[85]	91.2	85.2	93.5	89.0	[84]
3	<i>n</i> -butane	10 ¹	50.91	44.31	RCM	[86]	100.1	89.5	93.5	89.0	[84]
4	<i>n</i> -butane	10 ¹	32.58	43.41 ²	RCM	[87]	96.7	89.3	93.5	89.0	[84]
5	<i>n</i> -butane	10 ¹	28.32 ²	-	RCM	[88]	95.3	-	93.5	89.0	[84]
6	<i>n</i> -butane	20 ¹	10.37	9.53 ²	RCM	[87]	93.2	84.1	93.5	89.0	[84]
7	<i>n</i> -pentane	10 ¹	7.23	7.84 ²	RCM	[89]	64.4	61.9	61.7	62.6	[90]
8	<i>n</i> -pentane	10 ¹	6.68	7.12	RCM	[91]	60.9	58.8	61.7	62.6	[90]
9	<i>n</i> -hexane	15 ¹	2.84	2.53	ST	[92]	27.4	36.9	24.8	26.0	[93]
10	<i>n</i> -hexane	32 ³	-	1.01	ST	[92]	-	26.0	24.8	26.0	[93]
11	<i>n</i> -heptane	20 ¹	1.15	0.74	RCM	[94]	< 0.0	< 0.0	0.0	0.0	[3, 4]
12	<i>n</i> -heptane	10 ¹	3.38 ²	2.72 ²	RCM	[94]	17.5	9.6	0.0	0.0	[3, 4]
13	<i>n</i> -heptane	20	1.67 ²	0.90	ST	[95]	4.9	< 0.0	0.0	0.0	[3, 4]
14	<i>n</i> -heptane	40	0.56 ²	0.39 ²	ST	[95]	< 0.0	< 0.0	0.0	0.0	[3, 4]
15	<i>n</i> -heptane	40	0.60	0.55 ⁴	ST	[96]	< 0.0	< 0.0	0.0	0.0	[3, 4]
16	<i>n</i> -nonane	15 ¹	1.61	1.44	ST	[97]	< 0.0	< 0.0	< 0.0	< 0.0	[93]
17	<i>n</i> -octane	20 ¹	1.15	0.93	ST	[45]	< 0.0	< 0.0	< 0.0	< 0.0	[93]
18	<i>n</i> -decane	50	0.27 ²	0.34	ST	[98]	< 0.0	< 0.0	< 0.0	< 0.0	[99]
19	<i>n</i> -dodecane	20 ¹	0.91 ²	0.94	ST	[100]	< 0.0	< 0.0	< 0.0	< 0.0	[99]

Continued on next page

n-paraffins

Table 2: (continued) Predicted RON and MON with experimental IDT

S. No.	Fuel	P_0 (bar)	$\tau_{id,RON}$ (ms)	$\tau_{id,MON}$ (ms)	Device	τ_{id} Ref.	Predicted		Nominal		RON/MON Ref.
							RON	MON	RON	MON	
20	iso-butane	10 ¹	113.09	106.34 ²	RCM	[101]	103.4	93.8	100.1	96.8	[84]
21	iso-butane	20 ¹	19.8 ²	17.46 ²	RCM	[101]	100.1	90.0	100.1	96.8	[84]
22	iso-butane	15	31.10	27.21	RCM	[85]	100.0	90.3	100.1	96.8	[84]
23	iso-pentane	10 ¹	35.79	59.78	RCM	[89]	97.5	91.3	92.3	90.3	[90]
24	iso-pentane	10 ¹	28.96	41.80	RCM	[91]	95.5	89.0	92.3	90.3	[90]
25	iso-pentane	20 ¹	7.47	11.58 ²	RCM	[89]	87.3	86.4	92.3	90.3	[90]
26	neo-pentane	10 ¹	27.5 ²	19.40 ²	RCM	[89]	95.0	81.1	85.5	80.2	[93]
27	2-methylpentane	15 ¹	5.74 ²	9.59	RCM	[102]	68.5	79.0	73.4	73.5	[93]
28	3-methylpentane	15 ¹	6.60	9.33	RCM	[102]	73.6	78.5	74.5	74.3	[93]
29	2,2-dimethylbutane	15 ¹	17.75 ²	35.45 ²	RCM	[102]	94.8	91.9	91.8	93.4	[26]
30	2,3-dimethylbutane	15 ¹	95.94 ²	162.26 ²	RCM	[102]	104.6	96.3	105.8	94.3	[26]
31	2,2-dimethylpentane	15 ¹	15.95	32.70	RCM	[94]	93.4	91.4	93.0	96.0	[103]
32	2,3-dimethylpentane	15 ¹	20.81	38.83	RCM	[94]	96.6	92.3	91.1	88.5	[104]
33	2,4-dimethylpentane	15 ¹	10.00	13.06	RCM	[94]	85.2	83.4	83.1	83.8	[104]
34	3,3-dimethylpentane	15 ¹	10.36 ²	18.65	RCM	[94]	86.0	87.3	80.8	84.0	[105]
35	3-ethylpentane	15 ¹	4.70	6.81	RCM	[94]	59.7	72.3	65.0	69.3	[93]
36	2-methylhexane	15 ¹	2.55	2.89	RCM	[94]	18.0	43.6	42.4	46.3	[104]
37	2-methylhexane	40	0.84	0.90	ST	[106]	31.3	34.7	42.4	46.3	[104]
38	3-methylhexane	15 ¹	3.15	3.77	RCM	[94]	35.5	54.9	52.0	55.0	[93]

Continued on next page

Isoparaffins

Table 2: (continued) Predicted RON and MON with experimental IDT

S. No.	Fuel	P_0 (bar)	$\tau_{id,RON}$ (ms)	$\tau_{id,MON}$ (ms)	Device	τ_{id} Ref.	Predicted		Nominal		RON/MON Ref.
							RON	MON	RON	MON	
39	2-methylheptane	20 ¹	1.80	1.58 ²	ST	[45]	13.0	30.0	21.7	23.8	[93]
40	iso-octane	15 ⁵	43.88	54.69	RCM	[107]	102.0	93.8	100.0	100.0	[3, 4]
41	iso-octane	15	46.15	79.98 ⁶	RCM	[108]	102.2	94.9	100.0	100.0	[3, 4]
42	iso-octane	20	24.13 ²	36.11	RCM	[108]	101.4	94.0	100.0	100.0	[3, 4]
43	iso-octane	34	8.83	-	ST	[96]	100.2	-	100.0	100.0	[3, 4]
44	iso-octane	40	4.72	2.42 ⁴	ST	[96]	96.0	76.8	100.0	100.0	[3, 4]
45	Propene	40 ¹	42.00	8.00	RCM	[109]	105.7	94.6	100.2	83.3	[84]
46	1-butene	30	16.97 ²	5.53 ²	RCM	[110]	102.6	84.2	98.0	80.0	[103]
47	2-butene	30	23.38 ²	5.82	RCM	[110]	103.6	84.9	100.0	84.0	[103]
48	1-hexene	10 ⁷	11.97	9.46	RCM	[79]	80.8	67.1	76.4	63.4	[93]
49	2-hexene	10 ⁷	23.01	17.49	RCM	[79]	92.8	79.6	92.7	80.8	[93]
50	3-hexene	10 ⁷	75.98	53.14	RCM	[79]	102.0	90.6	94.0	80.1	[93]
51	iso-butene	30	52.84	15.22 ²	RCM	[111]	104.9	93.8	106.3	90.3	[112]
52	Cyclohexane	11 ³	16.25	17.73	RCM	[78]	87.4	79.8	83.0	77.2	[93]
53	Methylcyclohexane	10 ¹	23.87	19.17	RCM	[113]	93.3	80.9	74.8	71.1	[90]
54	Methylcyclohexane	15 ¹	8.21 ²	6.40	RCM	[113]	80.3	70.9	74.8	71.1	[90]
55	Methylcyclohexane	20 ¹	4.52	-	RCM	[113]	72.9	-	74.8	71.1	[90]
56	Methylcyclohexane	50 ¹	1.41	1.02 ⁴	ST	[114]	73.1	61.0	74.8	71.1	[90]
57	Methylcyclohexane	45 ¹	1.67 ⁴	1.26	ST	[115]	75.5	61.8	74.8	71.1	[90]
58	Methanol	24 ³	> 100	14.16 ⁴	RCM	[116]	> 105.6	90.6	122.0	93.0	[112]
59	Ethanol	35	-	5.15	RCM	[117]	-	86.7	109.0	90.0	[64]
60	Ethanol	40	63.10	3.97	RCM	[118]	106.0	86.7	109.0	90.0	[64]

Continued on next page

Table 2: (continued) Predicted RON and MON with experimental IDT

S. No.	Fuel	P_0 (bar)	$\tau_{id,RON}$ (ms)	$\tau_{id,MON}$ (ms)	Device	τ_{id} Ref.	Predicted		Nominal		RON/MON Ref.
							RON	MON	RON	MON	
61	Ethanol	50	5.45	1.63 ²	ST	[119]	100.3	80.1	109.0	90.0	[64]
62	1-propanol	35	123.51 ²	4.25	RCM	[117]	105.4	83.8	104.0	89.0	[120]
63	<i>n</i> -butanol	15	48.03 ⁴	22.82 ⁴	RCM	[121]	102.4	89.0	98.0	85.0	[120]
64	<i>n</i> -butanol	20	15.88 ⁴	7.16 ⁴	RCM	[82]	98.3	80.1	98.0	85.0	[120]
65	<i>s</i> -butanol	30	64.54	11.33	RCM	[122]	105.0	91.9	105.0	93.0	[120]
66	<i>i</i> -butanol	30	143.66 ⁴	13.42	RCM	[122]	105.4	93.1	105.0	90.0	[120]
67	<i>t</i> -butanol	30	58.01 ⁴	9.92 ⁴	RCM	[122]	104.9	90.8	107.0	94.0	[123]
68	<i>iso</i> -pentanol	20	25.03	9.82	RCM	[124]	101.6	84.5	113.0	88.0	[112]
69	1-hexanol	10 ⁸	10.00	17.22	RCM	[80]	75.8	79.3	69.3	78.0	[112]
70	<i>n</i> -octanol	20	2.34	1.78 ²	ST	[125]	36.7	36.8	28.0	27.0	[126]
71	<i>n</i> -octanol	40	0.85	0.74	ST	[125]	32.2	20.4	28.0	27.0	[126]
72	2-methyltetrahydrofuran	20	11.04	4.45	RCM/ST (HT)	[127]	94.1	70.7	88.2	71.2	[127]
73	2-methylfuran	20	-	13.60	ST	[127]	-	87.9	100.7	82.4	[127]
74	Methyl tert-butyl ether	24 ³	> 100	26.58 ⁴	RCM	[116]	> 105.6	94.2	118.0	101.0	[112]
75	<i>n</i> -propylbenzene	30 ^{1,9}	-	48.40	RCM	[81]	-	98.0	111.0	98.7	[93]
76	<i>n</i> -propylbenzene	50 ^{1,9}	25.56 ¹⁰	3.16	RCM	[81]	107.6	93.3	111.0	98.7	[93]
77	<i>n</i> -butylbenzene	30 ¹	26.50	13.32	RCM	[128]	103.9	93.0	104.4	95.3	[93]
78	<i>n</i> -butylbenzene	50 ¹	5.75 ²	-	RCM	[128]	100.8	-	104.4	95.3	[93]
79	Tetralin	35	47.86 ²	-	RCM	[129]	105.0	-	96.5	81.9	[112]

Continued on next page

Table 2: (continued) Predicted RON and MON with experimental IDT

S. No.	Fuel	P_0 (bar)	$\tau_{id,RON}$ (ms)	$\tau_{id,MON}$ (ms)	Device	τ_{id} Ref.	Predicted		Nominal		RON/MON Ref.
							RON	MON	RON	MON	
80	EoRON95 ¹¹	50	2.26	1.62	ST	[119]	87.0	79.9	94.7	85.7	[119]
81	FACE A	20	4.31	4.63	ST	[38]	71.1	71.6	83.5	83.6	[130]
82	FACE C	20	5.71	4.73	ST	[38]	80.6	72.1	84.7	83.6	[130]
83	FACE F	20 ¹	9.84	13.91	RCM	[42]	92.4	88.1	94.4	88.8	[130]
84	FACE G	20 ¹	14.93	13.91	RCM	[42]	97.7	88.1	96.8	85.8	[130]
85	Light naphtha	20	3.55	2.95	ST	[131]	62.6	58.7	64.5	63.5	[131]
86	Light naphtha	40	1.52	1.34	ST	[131]	68.2	56.6	64.5	63.5	[131]
87	PR5801 ¹¹	20	9.39	12.63	RCM	[82]	91.7	87.2	95.0	86.6	[82]
88	RD387 gasoline ¹¹	20	8.95	11.70 ²	RCM	[36]	90.8	86.5	91.0	82.7	[36]
89	E20SB ¹¹	50	4.31	1.68 ²	ST	[119]	97.8	81.0	101.6	88.5	[119]
90	E85SB ¹¹	50	4.90	1.76 ²	ST	[119]	99.2	82.3	107.0	89.3	[119]
91	ETBE20SB ¹¹	50	3.15	1.85	ST	[119]	93.4	83.6	99.9	89.1	[119]
92	I20SB ¹¹	50	3.11	1.53 ²	ST	[119]	93.2	78.1	98.8	86.8	[119]
93	M20SB ¹¹	50	5.64	2.05	ST	[119]	100.6	86.0	101.8	88.1	[119]
94	PRF 60	40	1.30 ⁴	1.38	ST	[96]	60.7	57.9	60.0	60.0	[3, 4]
95	PRF 70	20	3.98 ²	4.02 ²	ST	[132]	67.8	68.1	70.0	70.0	[3, 4]
96	PRF 70	40	1.44	1.42	ST	[132]	65.8	59.2	70.0	70.0	[3, 4]
97	PRF 80	20	-	4.50	ST	[132]	-	70.9	80.0	80.0	[3, 4]
98	PRF 80	40	1.91	1.98	ST	[132]	77.0	71.2	80.0	80.0	[3, 4]

Continued on next page

Table 2: (continued) Predicted RON and MON with experimental IDT

S. No.	Fuel	P_0 (bar)	$\tau_{id,RON}$ (ms)	$\tau_{id,MON}$ (ms)	Device	τ_{id} Ref.	Predicted		Nominal		RON/MON Ref.
							RON	MON	RON	MON	
99	PRF 80	40	1.93 ⁴	1.87 ⁴	ST	[96]	77.4	69.4	80.0	80.0	[3, 4]
100	PRF 84	20	4.60	4.79	ST	[38]	73.6	72.4	84.0	84.0	[3, 4]
101	PRF 90	15 ⁵	13.25	17.21	RCM	[107]	90.6	86.5	90.0	90.0	[3, 4]
102	PRF 90	40	3.13 ⁴	2.00	ST	[96]	89.7	71.6	90.0	90.0	[3, 4]
103	PRF 95	15 ⁵	23.64	30.14	RCM	[107]	97.9	90.9	95.0	95.0	[3, 4]
104	TRF 50	10 ⁷	7.01	5.42	RCM	[133]	63.1	48.6	66.6	58.4	[30]
105	TRF 60	10 ⁷	10.43	7.62	RCM	[133]	77.1	61.0	77.7	68.3	[30]
106	TRF 65	30	3.44 ⁴	2.82 ⁴	ST	[134]	84.6	70.8	84.0	73.2	[135]
107	TRF 65	50	1.83 ⁴	1.39 ⁴	ST	[134]	81.6	74.9	84.0	73.2	[135]
108	TRF 75	10 ⁷	42.56	30.28	RCM	[133]	98.9	86.3	93.3	81.9	[30]
109	TPRF-21-43	20	4.54	3.19	ST	[58]	73.1	61.3	70.0	66.0	[58]
110	TPRF-21-43	40	1.83 ²	1.47	ST	[58]	75.5	60.6	70.0	66.0	[58]
111	TPRF 23-11	20	9.22	11.23	RCM	[82]	91.4	86.0	95.0	89.8 ¹² /88.6 ¹³	[82]
112	TPRF-32-40	20	6.44	4.69	RCM/ST (HT)	[58]	83.9	71.9	80.4	75.3	[58]
113	TPRF-32-40	40	2.24 ¹⁴	1.65 ¹⁵	ST	[58]	81.9	65.1	80.4	75.3	[58]
114	TPRF-44-37	20	13.73	13.04	RCM	[58]	96.8	87.5	92.0	84.3	[58]
115	TPRF-44-37	40	3.41	2.18	ST	[58]	91.3	74.1	92.0	84.3	[58]
116	TPRF-70-12	20	35.54	23.85	RCM	[58]	103.2	92.0	98.0	87.1	[58]
117	TPRF-70-12	40	5.34 ¹⁶	2.39	RCM/ST (HT)	[58]	97.4	76.5	98.0	87.1	[58]

Continued on next page

Surrogates

Table 2: (continued) Predicted RON and MON with experimental IDT

S. No.	Fuel	P_0 (bar)	$\tau_{id,RON}$ (ms)	$\tau_{id,MON}$ (ms)	Device	τ_{id} Ref.	Predicted		Nominal		RON/MON Ref.
							RON	MON	RON	MON	
118	TPRF-45-25+10v.% DIB ¹⁷	30	7.22	4.09 ⁴	ST	[135]	97.1	79.2	94.6	85.0	[135]
119	EPRF-20-62	30	6.51	4.57	ST	[135]	96.0	82.0	95.1	89.5	[135]
120	ETPRF-40-12-38	30	5.31	-	ST	[136]	93.3	-	98.8	-	[136]
121	ETPRF-40-12-38	50	4.45 ²	-	ST	[136]	98.2	-	98.8	-	[136]

¹ Actual measurement in atm, approximated as bar in the present ¹⁰ IDT at 800 K as opposed to 820 K

work

² Linearly interpolated IDT

³ RON and MON predicted with interpolated n and coefficients

⁴ IDT obtained from trendlines in figures of corresponding Ref.

⁵ Actual measurement pressure 12-17 bar, approximated as 15 bar [78]

⁶ IDT at 790 K as opposed to 800 K

⁷ Actual measurement pressure 7.95-10.38 bar, approximated as 10 bar [79]

⁸ Actual measurement pressure 9 bar, approximated as 10 bar [80]

⁹ Actual measurement at $\phi = 0.96$, approximated as $\phi = 1.0$ [81]

¹¹ For details on fuels and its composition please refer to corresponding Refs.

¹² MON estimated in [82] with linear blending rule law

¹³ MON calculated with empirical correlations in [30] and used in present work

¹⁴ IDT at 810 K as opposed to 790 K

¹⁵ IDT at 885 K as opposed to 900 K

¹⁶ IDT at 780 K as opposed to 790 K

¹⁷ Diisobutylene (2,4,4-trimethyl-1-pentene)

Figure 9: Comparison between predicted and nominal RON/MON with experimental IDT in Table 2

3.4 Validation with condition “beyond RON”

As pressure/temperature history in modern SI engines have deviated from typical conditions in CFR engines [59, 10, 48, 137], it is imperative to identify conditions in homogeneous reactors that are relevant to such modern SI engines. It should be noted that while end-gas autoignition near the peak cylinder temperature and pressure, the chemical reactions leading to ignition start much earlier. It is not unrealistic to expect that the end-gas partially reacts at 600–700 K during the compression stroke and while the flame is propagating. The partially reacted mixture will have modified chemistry at the time of ignition. The understanding of autoignition chemistry at these conditions could provide insights on tailoring future fuels for such engines.

For quantitative evaluations of the antiknock quality of fuels at conditions “beyond RON”, correlations were developed with the same methodology as discussed above. With RON-like and MON-like temperatures given in Table 1, the temperatures corresponding to $k = 0.5$, -0.5 and -1.0 were determined by linear interpolation and extrapolation to obtain temperatures where IDT could be related with AKI ($k = 0.5$), and OI (at $k = -0.5, -1.0$). From the previously obtained 31 set of coefficients and exponents, i.e., correlations with IDT in the same functional form as Eq. (2), the coefficients and exponents a , b and n corresponding to these temperatures were obtained

and used in estimating AKI ($k = 0.5$), and OI (at $k = -0.5, -1.0$) with IDT of TRFs and TPRFs at the same temperatures. The exponent and coefficients for $k = 0.5, -0.5$ and -1.0 is given in Tables 3 and 4. Comparisons with predicted and nominal OI at different k values are shown in Fig. 10. Panel 10(a) shows predicted AKI, i.e., at $k = 0.5$ at 40 bar with the nominal values, while panel 10(b) shows predicted values at $k = -0.5$ at 20 bar and panel 10(c) shows $k = -1.0$ at 45 bar. It can be observed that the high R^2 values indicate great degree of accuracy in predicting OI at these conditions, which enables future IDT measurements to be focused on conditions relevant to modern SI engines.

Table 3: Exponent n and coefficients a, b in Eq. (2) to predict AKI.

P_0 [bar]	T_0 [K]	n	a	b
10	750	0.90	-230.34	103.04
15	770	0.92	-150.67	103.25
20	790	0.91	-108.84	103.74
25	800	0.93	-86.87	103.87
30	820	0.90	-70.81	104.67
35	830	0.90	-60.36	105.01
40	850	0.86	-54.13	106.33
45	870	0.83	-50.78	108.22
50	880	0.84	-46.05	108.86
55	900	0.85	-44.26	111.12
60	920	0.89	-41.72	113.44

Table 4: Exponent n and coefficients a, b in Eq. (2) to predict OI.

P_0 [bar]	$k = -1.0$				$k = -0.5$			
	T_0 [K]	n	a	b	T_0 [K]	n	a	b
10	-	-	-	-	710	-1.06	-482.06	112.39
15	-	-	-	-	710	-1.28	-558.90	111.97
20	-	-	-	-	720	-1.35	-420.47	111.94
25	-	-	-	-	720	-1.49	-452.25	111.79
30	-	-	-	-	730	-1.48	-308.31	112.06
35	-	-	-	-	730	-1.58	-316.35	111.98
40	-	-	-	-	740	-1.56	-217.71	112.11
45	700	-1.83	-1340.68	117.56	750	-1.52	-151.98	112.45
50	710	-1.80	-800.67	117.73	760	-1.48	-109.87	112.76
55	720	-1.77	-491.01	117.93	780	-1.32	-67.22	113.45
60	750	-1.55	-145.16	118.48	800	-1.19	-48.21	114.19

Figure 10: Comparison between predicted and nominal OI at (a) $P_0 = 40$ bar and $k = 0.5$ (AKI) (b) $P_0 = 20$ bar and $k = -0.5$ (c) $P_0 = 45$ bar and $k = -1.0$

4 UNCERTAINTY ANALYSIS

IDT measurements in ST and RCM are subject to uncertainties from several sources, which stem from uncertainties in pressure, temperature, and mixture composition. Details on uncertainties in ignition delay measurements in ST and RCM are available in [76, 138]. Note that these uncertainties are not random errors, but systematic errors that arise due to facility effects. A detailed uncertainty analysis of the chemical kinetic model used requires the use of Monte Carlo techniques and Bayesian-like methods: minimization using polynomial chaos expansion. The application of such techniques

Table 5: Uncertainty in coefficients a , b in Eq. (2) to predict RON and MON

P_0 [bar]	RON		MON	
	a	b	a	b
10	296.01 ± 40.89	106.11 ± 2.31	206.26 ± 26.32	97.68 ± 2.09
15	234.57 ± 34.64	106.60 ± 2.56	138.00 ± 18.31	97.83 ± 2.21
20	179.68 ± 28.35	106.62 ± 2.75	101.85 ± 13.68	98.45 ± 2.35
25	132.07 ± 21.89	106.10 ± 2.79	85.05 ± 11.70	99.32 ± 2.55
30	95.91 ± 16.22	105.58 ± 2.73	74.92 ± 10.79	100.29 ± 2.84
35	73.28 ± 12.16	105.64 ± 2.67	67.81 ± 10.37	101.47 ± 3.24
40	61.85 ± 9.89	106.59 ± 2.76	61.22 ± 10.24	102.59 ± 3.77
45	56.32 ± 8.79	108.05 ± 2.99	53.35 ± 10.20	103.15 ± 4.47
50	51.65 ± 7.92	109.45 ± 3.24	43.19 ± 9.89	103.10 ± 5.42

and methods is beyond the scope of the present work. A simplified approach was following where we assumed that IDT calculated from chemical kinetic simulations have a worst case uncertainty of 100%. The uncertainty in ON measurement was taken as the reproducibility limit for RON, i.e., 1.2 [3]. For the uncertainty in IDT and ON measurement, the uncertainty in the predictions of fit parameters and the ON obtained with Eq. (2) was calculated with [139], which predicted the uncertainty by linear error propagation theory. The uncertainties in fit parameters are shown in Table 5. The uncertainty in predictions of ON considering the uncertainties stated above are shown in Fig. S20, indicated by the prediction band. The uncertainties in ON prediction at other pressures are shown in Fig. S22.

The uncertainty in the prediction of RON/MON with uncertainties relevant to practical devices is discussed here. Uncertainties associated with ignition delay measurements are typically in the range of 10–20% [138, 140, 141]. Assuming a maximum uncertainty of $\pm 20\%$ together with the uncertainties in the fit parameters given in Table 5, the uncertainties associated with estimation of RON and MON at 20 and 40 bar are shown in Fig. 11. Uncertainties in the estimation of RON and MON at different pressures with $\pm 20\%$ uncertainty in IDT is given in Fig. S22. As can be observed, large uncertainties occur in the lower ON range due to steeper variation of ON with IDT. However, for longer IDT, where most uncertainties in measurements occur due to departure from idealities, the uncertainty in RON/MON estimations are very low. In the range of ON measurements. i.e., 40–100 the average uncertainties of RON/MON predictions were calculated to be $\pm 4.0/3.2$ and $\pm 3.8/4.3$ at 20 and 40 bar, respectively. The lower uncertainties in the higher ON range make the method ideal for estimating ON of gasoline like fuels, however, for reactive fuels the estimations are subject to large uncertainties.

Figure 11: Uncertainty in estimation of (a) RON and (b) MON (bottom) at 20 and 40 bar for $\pm 20\%$ uncertainty in IDT. Inset represents higher ON range.

5 CONCLUDING REMARKS

This work presents correlations of RON and MON with homogeneous gas-phase IDT at different pressures. The basic premise of this work is that at specific conditions of pressure and temperature, the IDT of a PRF and its RON/MON are correlated. The correlations were developing using IDT simulations of PRF using the KAUST-LLNL-NUIG gasoline surrogate chemical kinetic model. The correlations obtained with PRF were then tested using simulated IDT from other chemical kinetic models, and similar trends in various models demonstrated the broad applicability and robustness of the present methodology. The correlations were also extended to predict RON and MON of TRF, TPRF, ERF, EPRF, ETPRF, and multicomponent surrogate mixtures. The RON and MON predicted with the correlations showed a reasonable level of accuracy, making it appropriate as first approximation of a fuel's antiknock quality.

As all the RONs and MONs were predicted with IDT calculated from chemical kinetic models, it was imperative to test the correlations with experimentally obtained IDT from literature data. The correlations, when applied to experimental IDT from literature, were able to predict RONs and MON with reasonable accuracy. Equations to predict IDT for a fuel with given RON and MON are also provided, which provides an idea on the ignition delay a fuel would have at RON- like and MON-like conditions at

different pressures. During the course of this work, a large amount of data at RON-like and MON- like conditions was not available, particularly at RON-like conditions, as these fall in the low temperature regime which has gathered considerable interest in recent years. In some cases, IDT at the exact RON-like and MON-like conditions were not available, hence had to be interpolated to validate the correlations. Future measurements of IDT at the proposed RON-like and MON-like conditions would be highly beneficial in evaluating RON/MON and thereby sensitivity, as modern trends of downsizing and turbocharging spark-ignition engines demand fuels that have lower MON for a given RON. Uncertainty analysis was also carried out to assess uncertainties in estimating RON/MON with experimentally obtained IDT. For long IDTs, the uncertainties associated with RON/MON estimation were low in comparison to the large uncertainties that could occur during experimental measurements.

ACKNOWLEDGMENTS

The research reported in this paper was funded by Saudi Aramco and the Clean Combustion Research Center at King Abdullah University of Science and Technology under the FUELCOM program.

REFERENCES

- [1] G. T. Kalghatgi, Fuel/engine interactions, SAE Internationaldoi:10.4271/R-409.
- [2] G. Edgar, Measurement of knock characteristics of gasoline in terms of a standard fuel, *Industrial & Engineering Chemistry* 19 (1) (1927) 145–146. doi:10.1021/ie50205a049.
- [3] ASTM D2699-13b, Standard test method for research octane number of spark-ignition engine fuel, ASTM Internationaldoi:10.1520/D2699.
- [4] ASTM D2700-16, Standard test method for motor octane number of spark-ignition engine fuel, ASTM Internationaldoi:10.1520/D2700-16.
- [5] J. Griffiths, Negative temperature-coefficient of reaction rate during hydrocarbon oxidation, *Journal of the Chemical Society D: Chemical Communications* (9) (1969) 483b–484. doi:10.1039/C2969000483B.
- [6] I. A. Leenson, G. B. Sergeev, Negative temperature coefficient in chemical reactions, *Russian Chemical Reviews* 53 (5) (1984) 417–434. doi:10.1070/RC1984v053n05ABEH003060.
- [7] W. R. Leppard, The chemical origin of fuel octane sensitivity, SAE Technical paper 902137. doi:10.4271/902137.
- [8] G. T. Kalghatgi, Fuel anti-knock quality - Part I. Engine studies, SAE Technical Paper 2001-01-3584. doi:10.4271/2001-01-3584.
- [9] G. T. Kalghatgi, Fuel anti-knock quality - Part II. Vehicle studies-how relevant is motor octane number MON in modern engines?, SAE Technical Paper 2001-01-3585. doi:10.4271/2001-01-3585.
- [10] V. Mittal, J. B. Heywood, The shift in relevance of fuel RON and MON to knock onset in modern SI engines over the last 70 years, *SAE International Journal of Engines* 2 (2009-01-2622) (2009) 1–10. doi:10.4271/2009-01-2622.
- [11] W. G. Lovell, J. M. Campbell, T. A. Boyd, Detonation characteristics of some paraffin hydrocarbons, *Industrial & Engineering Chemistry* 23 (1) (1931) 26–29. doi:10.1021/ie50253a015.
- [12] W. G. Lovell, J. M. Campbell, T. A. Boyd, Detonation characteristics of some aliphatic olefin hydrocarbons, *Industrial & Engineering Chemistry* 23 (5) (1931) 555–558. doi:10.1021/ie50257a021.
- [13] W. G. Lovell, J. M. Campbell, T. A. Boyd, Knocking characteristics of naphthene hydrocarbons, *Industrial & Engineering Chemistry* 25 (10) (1933) 1107–1110. doi:10.1021/ie50286a011.

- [14] W. G. Lovell, J. M. Campbell, T. A. Boyd, Knocking characteristics of hydrocarbons determined from compression ratios at which individual compounds begin to knock under specified conditions, *Industrial & Engineering Chemistry* 26 (10) (1934) 1105–1108. doi:10.1021/ie50298a019.
- [15] W. G. Lovell, Knocking characteristics of hydrocarbons, *Industrial & Engineering Chemistry* 40 (12) (1948) 2388–2438. doi:10.1021/ie50468a033.
- [16] D. Downs, A. D. Walsh, R. W. Wheeler, A study of the reactions that lead to ‘knock’ in the spark-ignition engine, *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences* 243 (870) (1951) 463–524. doi:10.1098/rsta.1951.0009.
- [17] D. Downs, S. Griffiths, R. Wheeler, Preflame reactions in the spark ignition engine. the influence of TEL and other antiknocks, *J. Inst. Petrol* 49 (469) (1963) 8.
- [18] A. J. Pahnke, P. M. Cohen, B. M. Sturgis, Preflame oxidation of hydrocarbons in a motored engine, *Industrial & Engineering Chemistry* 46 (5) (1954) 1024–1029. doi:10.1021/ie50533a058.
- [19] C. Walcutt, J. M. Mason, E. Rifkin, Effect of preflame oxidation reactions on engine knock, *Industrial & Engineering Chemistry* 46 (5) (1954) 1029–1034. doi:10.1021/ie50533a059.
- [20] A. Walsh, The knock ratings of fuels, in: *Symposium (International) on Combustion*, Vol. 9, Elsevier, 1963, pp. 1046–1055. doi:10.1016/S0082-0784(63)80110-1.
- [21] C. K. Westbrook, W. J. Pitz, W. R. Leppard, The autoignition chemistry of paraffinic fuels and pro-knock and anti-knock additives: a detailed chemical kinetic study, *SAE Technical Paper* 912314. doi:10.4271/912314.
- [22] P. C. Anderson, J. M. Sharkey, R. P. Walsh, Calculation of the research octane number of motor gasolines from gas chromatographic data and a new approach to motor gasoline quality control, *Journal of the Institute of Petroleum* 58 (560) (1972) 83.
- [23] M. E. Myers Jr, J. Stollsteimer, A. M. Wims, Determination of gasoline octane numbers from chemical composition, *Analytical Chemistry* 47 (13) (1975) 2301–2304. doi:10.1021/ac60363a015.
- [24] J. J. Kelly, C. H. Barlow, T. M. Jinguji, J. B. Callis, Prediction of gasoline octane numbers from near-infrared spectral features in the range 660–1215 nm, *Analytical Chemistry* 61 (4) (1989) 313–320. doi:10.1021/ac00179a007.

- [25] J. A. Van Leeuwen, R. J. Jonker, R. Gill, Octane number prediction based on gas chromatographic analysis with non-linear regression techniques, *Chemo-metrics and intelligent laboratory systems* 25 (2) (1994) 325–340. doi:10.1016/0169-7439(94)85051-8.
- [26] P. Ghosh, K. J. Hickey, S. B. Jaffe, Development of a detailed gasoline composition-based octane model, *Industrial & engineering chemistry research* 45 (1) (2006) 337–345. doi:10.1021/ie050811h.
- [27] W. Pitz, N. Cernansky, F. Dryer, F. Egolfopoulos, J. Farrell, D. Friend, H. Pitsch, Development of an experimental database and chemical kinetic models for surrogate gasoline fuels, *SAE technical paper* (2007-01-0175) (2007) 0175. doi:10.4271/2007-01-0175.
- [28] T. Wallington, E. Kaiser, J. Farrell, Automotive fuels and internal combustion engines: a chemical perspective, *Chemical Society Reviews* 35 (4) (2006) 335–347. doi:10.1039/B410469M.
- [29] N. Morgan, A. Smallbone, A. Bhawe, M. Kraft, R. Cracknell, G. Kalghatgi, Mapping surrogate gasoline compositions into RON/MON space, *Combustion and Flame* 157 (6) (2010) 1122–1131. doi:10.1016/j.combustflame.2010.02.003.
- [30] G. Kalghatgi, H. Babiker, J. Badra, A simple method to predict knock using toluene, iso-octane, n-heptane blends (TPRF) as gasoline surrogates, *SAE International Journal of Engines* 7 (2015) 663–672. doi:10.4271/2015-01-0757.
- [31] A. S. AlRamadan, S. M. Sarathy, M. Khurshid, J. Badra, A blending rule for octane numbers of PRFs and TPRFs with ethanol, *Fuel* 180 (2016) 175–186. doi:10.1016/j.fuel.2016.04.032.
- [32] E. Singh, J. Badra, M. Mehl, S. M. Sarathy, Chemical kinetic insights into the octane number and octane sensitivity of gasoline surrogate mixtures, *Energy & Fuels* 31 (2) (2017) 1945–1960. doi:10.1021/acs.energyfuels.6b02659.
- [33] G. Kalghatgi, R. Head, J. Chang, Y. Viollet, H. Babiker, A. Amer, An alternative method based on toluene/n-heptane surrogate fuels for rating the anti-knock quality of practical gasolines, *SAE International Journal of Fuels and Lubricants* 2014-01-2609. doi:10.4271/2014-01-2609.
- [34] T. M. Foong, K. J. Morganti, M. J. Brear, G. da Silva, Y. Yang, F. L. Dryer, The octane numbers of ethanol blended with gasoline and its surrogates, *Fuel* 115 (2014) 727–739. doi:10.1016/j.fuel.2013.07.105.
- [35] 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 (11) (2011) 5215–5223. doi:10.1021/ef201099y.
- [36] G. Kukkadapu, K. Kumar, C.-J. Sung, M. Mehl, W. J. Pitz, Experimental and surrogate modeling study of gasoline ignition in a rapid compression machine, *Combustion and Flame* 159 (10) (2012) 3066–3078. doi:10.1016/j.combustflame.2012.05.008.
- [37] G. Kukkadapu, K. Kumar, C.-J. Sung, M. Mehl, W. J. Pitz, Autoignition of gasoline and its surrogates in a rapid compression machine, *Proceedings of the Combustion Institute* 34 (1) (2013) 345–352. doi:10.1016/j.proci.2012.06.135.
- [38] S. M. Sarathy, G. Kukkadapu, M. Mehl, W. Wang, T. Javed, S. Park, M. A. Oehlschlaeger, A. Farooq, W. J. Pitz, C.-J. Sung, Ignition of alkane-rich FACE gasoline fuels and their surrogate mixtures, *Proceedings of the Combustion Institute* 35 (1) (2015) 249–257. doi:10.1016/j.proci.2014.05.122.
- [39] K. Anand, Y. Ra, R. Reitz, B. Bunting, Surrogate model development for fuels for advanced combustion engines, *Energy & Fuels* 25 (4) (2011) 1474–1484. doi:10.1021/ef101719a.
- [40] A. Ahmed, G. Goteng, V. S. Shankar, K. Al-Qurashi, W. L. Roberts, S. M. Sarathy, A computational methodology for formulating gasoline surrogate fuels with accurate physical and chemical kinetic properties, *Fuel* 143 (2015) 290–300. doi:10.1016/j.fuel.2014.11.022.
- [41] Y. Ra, R. D. Reitz, A combustion model for multi-component fuels using a physical surrogate group chemistry representation (PSGCR), *Combustion and Flame* 162 (10) (2015) 3456–3481. doi:10.1016/j.combustflame.2015.05.014.
- [42] S. M. Sarathy, G. Kukkadapu, M. Mehl, T. Javed, A. Ahmed, N. Naser, A. Tekawade, G. Kosiba, M. AlAbbad, E. Singh, et al., Compositional effects on the ignition of FACE gasolines, *Combustion and Flame* 169 (2016) 171–193. doi:10.1016/j.combustflame.2016.04.010.
- [43] C. K. Westbrook, M. Mehl, W. J. Pitz, M. Sjöberg, Chemical kinetics of octane sensitivity in a spark-ignition engine, *Combustion and Flame* 175 (2017) 2–15. doi:10.1016/j.combustflame.2016.05.022.
- [44] J. Griffiths, P. Halford-Maw, C. Mohamed, Spontaneous ignition delays as a diagnostic of the propensity of alkanes to cause engine knock, *Combustion and flame* 111 (4) (1997) 327–337. doi:10.1016/S0010-2180(97)00004-7.
- [45] S. M. Sarathy, T. Javed, F. Karsenty, A. Heufer, W. Wang, S. Park, A. Elwardany, A. Farooq, C. K. Westbrook, W. J. Pitz, M. A. Oehlschlaeger, G. Dayma,

- H. J. Curran, P. Dagaut, A comprehensive combustion chemistry study of 2,5-dimethylhexane, *Combustion and Flame* 161 (6) (2014) 1444–1459. doi:10.1016/j.combustflame.2013.12.010.
- [46] J. A. Badra, N. Bokhumseen, N. Mulla, S. M. Sarathy, A. Farooq, G. Kalghatgi, P. Gaillard, A methodology to relate octane numbers of binary and ternary n-heptane, iso-octane and toluene mixtures with simulated ignition delay times, *Fuel* 160 (2015) 458–469. doi:10.1016/j.fuel.2015.08.007.
- [47] D. Bradley, R. A. Head, Engine autoignition: The relationship between octane numbers and autoignition delay times, *Combustion and Flame* 147 (3) (2006) 171–184. doi:10.1016/j.combustflame.2006.09.001.
- [48] N. Naser, S. Y. Yang, G. Kalghatgi, S. H. Chung, Relating the octane numbers of fuels to ignition delay times measured in an ignition quality tester (IQT), *Fuel* 187 (2017) 117–127. doi:10.1016/j.fuel.2016.09.013.
- [49] T. Lu, C. K. Law, Toward accommodating realistic fuel chemistry in large-scale computations, *Progress in Energy and Combustion Science* 35 (2) (2009) 192–215. doi:10.1016/j.pecs.2008.10.002.
- [50] G. Shibata, T. Urushihara, Auto-ignition characteristics of hydrocarbons and development of HCCI fuel index, Tech. rep., SAE Technical Paper (2007). doi:10.4271/2007-01-0220.
- [51] V. H. Rapp, W. J. Cannella, J.-Y. Chen, R. W. Dibble, Predicting fuel performance for future HCCI engines, *Combustion Science and Technology* 185 (5) (2013) 735–748. doi:10.1080/00102202.2012.750309.
- [52] I. Truedsson, W. Cannella, B. Johansson, M. Tuner, Development of new test method for evaluating HCCI fuel performance, Tech. rep., SAE Technical Paper (2014). doi:10.4271/2014-01-2667.
- [53] K. E. Niemeyer, S. R. Daly, W. J. Cannella, C. L. Hagen, A novel fuel performance index for low-temperature combustion engines based on operating envelopes in light-duty driving cycle simulations, *Journal of Engineering for Gas Turbines and Power* 137 (10) (2015) 101601. doi:10.1115/1.4029948.
- [54] K. E. Niemeyer, S. R. Daly, W. J. Cannella, C. L. Hagen, Investigation of the LTC fuel performance index for oxygenated reference fuel blends, *Fuel* 155 (2015) 14–24. doi:10.1016/j.fuel.2015.04.010.
- [55] M. Waqas, N. Naser, M. Sarathy, K. Morganti, K. Al-Qurashi, B. Johansson, Blending octane number of ethanol in HCCI, SI and CI combustion modes, *SAE International Journal of Fuels and Lubricants* 9 (2016-01-2298) (2016) 659–682.

- [56] T. M. Foong, M. J. Brear, K. J. Morganti, G. da Silva, Y. Yang, F. L. Dryer, Modeling end-gas autoignition of ethanol/gasoline surrogate blends in the cooperative fuel research engine, *Energy & Fuels* 31 (3) (2017) 2378–2389. doi:10.1021/acs.energyfuels.6b02380.
- [57] G. T. Kalghatgi, Auto-ignition quality of practical fuels and implications for fuel requirements of future SI and HCCI engines, SAE Technical Paper 2005-01-0239. doi:10.4271/2005-01-0239.
- [58] T. Javed, C. Lee, M. AlAbbad, K. Djebbi, M. Beshir, J. Badra, H. Curran, A. Farooq, Ignition studies of n-heptane/iso-octane/toluene blends, *Combustion and Flame* 171 (2016) 223–233. doi:10.1016/j.combustflame.2016.06.008.
- [59] M. Mehl, T. Faravelli, F. Giavazzi, E. Ranzi, P. Scorletti, A. Tardani, D. Terna, Detailed chemistry promotes understanding of octane numbers and gasoline sensitivity, *Energy & fuels* 20 (6) (2006) 2391–2398. doi:10.1021/ef060339s.
- [60] D. Goodwin, H. K. Moffat, R. L. Speth, Cantera: An object-oriented software toolkit for chemical kinetics, thermodynamics and transport processes, 2009, <http://www.cantera.org/>.
- [61] M. Mehl, W. J. Pitz, C. K. Westbrook, H. J. Curran, Kinetic modeling of gasoline surrogate components and mixtures under engine conditions, *Proceedings of the Combustion Institute* 33 (1) (2011) 193–200. doi:10.1016/j.proci.2010.05.027.
- [62] L. Cai, H. Pitsch, Optimized chemical mechanism for combustion of gasoline surrogate fuels, *Combustion and Flame* 162 (5) (2015) 1623–1637. doi:10.1016/j.combustflame.2014.11.018.
- [63] A. Frassoldati, A. Cuoci, T. Faravelli, E. Ranzi, Kinetic modeling of the oxidation of ethanol and gasoline surrogate mixtures, *Combustion Science and Technology* 182 (4-6) (2010) 653–667. doi:10.1080/00102200903466368.
- [64] I. Hunwartz, Modification of CFR test engine unit to determine octane numbers of pure alcohols and gasoline-alcohol blends, SAE Technical Paper 820002. doi:10.4271/820002.
- [65] T. M. Foong, K. J. Morganti, M. J. Brear, G. da Silva, Y. Yang, F. L. Dryer, The effect of charge cooling on the RON of ethanol/gasoline blends, *SAE International Journal of Fuels and Lubricants* 6 (2013-01-0886) (2013) 34–43. doi:10.4271/2013-01-0886.
- [66] E. Kasseris, J. B. Heywood, Charge cooling effects on knock limits in SI DI engines using gasoline/ethanol blends: Part 1-Quantifying charge cooling 2012-01-1275. doi:10.4271/2012-01-1275.

- [67] E. Kasseris, J. B. Heywood, Charge cooling effects on knock limits in SI DI engines using gasoline/ethanol blends: Part 2-Effective octane numbers, *SAE International Journal of Fuels and Lubricants* 5 (2012-01-1284) (2012) 844–854. doi:10.4271/2012-01-1284.
- [68] R. A. Stein, D. Polovina, K. Roth, M. Foster, M. Lynskey, T. Whiting, J. E. Anderson, M. H. Shelby, T. G. Leone, S. VanderGriend, Effect of heat of vaporization, chemical octane, and sensitivity on knock limit for ethanol-gasoline blends, *SAE International Journal of Fuels and Lubricants* 5 (2012-01-1277) (2012) 823–843. doi:10.4271/2012-01-1277.
- [69] C. S. Sluder, J. P. Szybist, R. L. McCormick, M. A. Ratcliff, B. T. Zigler, Exploring the relationship between octane sensitivity and heat-of-vaporization, *SAE International Journal of Fuels and Lubricants* 9 (2016-01-0836) (2016) 80–90. doi:10.4271/2016-01-0836.
- [70] J. P. Szybist, D. A. Splitter, Pressure and temperature effects on fuels with varying octane sensitivity at high load in SI engines, *Combustion and Flame* 177 (2017) 49–66. doi:10.1016/j.combustflame.2016.12.002.
- [71] G. T. Kalghatgi, K. Nakata, K. Mogi, Octane appetite studies in direct injection spark ignition DISI engines, *SAE Technical Paper* 2005-01-0244. doi:10.4271/2005-01-0244.
- [72] V. Mittal, J. B. Heywood, The relevance of fuel RON and MON to knock onset in modern SI engines, *SAE Technical Paper* 2008-01-2414. doi:10.4271/2008-01-2414.
- [73] D. Davidson, R. Hanson, Interpreting shock tube ignition data, *International Journal of Chemical Kinetics* 36 (9) (2004) 510–523. doi:10.1002/kin.20024.
- [74] E. L. Petersen, R. K. Hanson, Nonideal effects behind reflected shock waves in a high-pressure shock tube, *Shock Waves* 10 (6) (2001) 405–420. doi:10.1007/PL00004051.
- [75] M. Chaos, F. L. Dryer, Chemical-kinetic modeling of ignition delay: Considerations in interpreting shock tube data, *International Journal of Chemical Kinetics* 42 (3) (2010) 143–150. doi:10.1002/kin.20471.
- [76] C.-J. Sung, H. J. Curran, Using rapid compression machines for chemical kinetics studies, *Progress in Energy and Combustion Science* 44 (2014) 1–18. doi:10.1016/j.pecs.2014.04.001.
- [77] D. Bradley, M. Lawes, M. Materego, Interpretation of auto-ignition delay times measured in different rapid compression machines, in: 25th International Collo-

quium on the Dynamics of Explosions and Reactive systems, Leeds, 2015.
URL <http://eprints.whiterose.ac.uk/87762/>

- [78] O. Lemaire, M. Ribaucour, M. Carlier, R. Minetti, The production of benzene in the low-temperature oxidation of cyclohexane, cyclohexene, and cyclohexa-1,3-diene, *Combustion and flame* 127 (1) (2001) 1971–1980. doi:10.1016/S0010-2180(01)00301-7.
- [79] G. Vanhove, M. Ribaucour, R. Minetti, On the influence of the position of the double bond on the low-temperature chemistry of hexenes, *Proceedings of the Combustion Institute* 30 (1) (2005) 1065–1072. doi:10.1016/j.proci.2004.08.042.
- [80] K. Heufer, J. Bugler, H. Curran, A comparison of longer alkane and alcohol ignition including new experimental results for n-pentanol and n-hexanol, *Proceedings of the Combustion Institute* 34 (1) (2013) 511–518. doi:10.1016/j.proci.2012.05.103.
- [81] D. Darcy, H. Nakamura, C. J. Tobin, M. Mehl, W. K. Metcalfe, W. J. Pitz, C. K. Westbrook, H. J. Curran, A high-pressure rapid compression machine study of n-propylbenzene ignition, *Combustion and Flame* 161 (1) (2014) 65–74. doi:10.1016/j.combustflame.2013.08.001.
- [82] E. Agbro, A. S. Tomlin, M. Lawes, S. Park, S. M. Sarathy, The influence of n-butanol blending on the ignition delay times of gasoline and its surrogate at high pressures, *Fuel* 187 (2017) 211–219. doi:10.1016/j.fuel.2016.09.052.
- [83] S. M. Gallagher, H. J. Curran, W. Metcalfe, D. Healy, J. M. Simmie, G. Bourque, A rapid compression machine study of the oxidation of propane in the negative temperature coefficient regime, *Combustion and Flame* 153 (1) (2008) 316–333. doi:10.1016/j.combustflame.2007.09.004.
- [84] K. J. Morganti, T. M. Foong, M. J. Brear, G. da Silva, Y. Yang, F. L. Dryer, The research and motor octane numbers of liquefied petroleum gas (LPG), *Fuel* 108 (2013) 797–811. doi:10.1016/j.fuel.2013.01.072.
- [85] S. Gersen, A. V. Mokhov, J. Darneveil, H. B. Levinsky, Ignition properties of n-butane and iso-butane in a rapid compression machine, *Combustion and Flame* 157 (2) (2010) 240–245. doi:10.1016/j.combustflame.2009.10.012.
- [86] J. F. Griffiths, P. A. Halford-Maw, D. J. Rose, Fundamental features of hydrocarbon autoignition in a rapid compression machine, *Combustion and flame* 95 (3) (1993) 291–306. doi:10.1016/0010-2180(93)90133-N.

- [87] D. Healy, N. Donato, C. Aul, E. Petersen, C. Zinner, G. Bourque, H. Curran, n-butane: Ignition delay measurements at high pressure and detailed chemical kinetic simulations, *Combustion and Flame* 157 (8) (2010) 1526–1539. doi:10.1016/j.combustflame.2010.01.016.
- [88] R. Minetti, M. Ribaucour, M. Carlier, C. Fittschen, L. R. Sochet, Experimental and modeling study of oxidation and autoignition of butane at high pressure, *Combustion and Flame* 96 (3) (1994) 201–211. doi:10.1016/0010-2180(94)90009-4.
- [89] J. Bugler, B. Marks, O. Mathieu, R. Archuleta, A. Camou, C. Grégoire, K. A. Heufer, E. L. Petersen, H. J. Curran, An ignition delay time and chemical kinetic modeling study of the pentane isomers, *Combustion and Flame* 163 (2016) 138–156. doi:10.1016/j.combustflame.2015.09.014.
- [90] A. De Klerk, *Fischer-Tropsch Refining*, John Wiley & Sons, 2012. doi:10.1002/9783527635603.
- [91] B. Marks, O. Mathieu, R. Archuleta, E. L. Petersen, J. Bugler, A. Heufer, H. J. Curran, Ignition delay time measurements and modeling of n-pentane and iso-pentane at elevated pressures, in: *51st AIAA Aerospace Sciences Meeting including the New Horizons Forum and Aerospace Exposition*, 2013, p. 160. doi:10.2514/6.2013-160.
- [92] K. Zhang, C. Banyon, C. Togbé, P. Dagaut, J. Bugler, H. J. Curran, An experimental and kinetic modeling study of n-hexane oxidation, *Combustion and Flame* 162 (11) (2015) 4194–4207. doi:10.1016/j.combustflame.2015.08.001.
- [93] J. C. Guibet, *Carburants et moteurs*, tome 1 et 2, publications de l'Institut Français du Pétrole, ed, Technip, Paris.
- [94] E. J. Silke, H. J. Curran, J. M. Simmie, The influence of fuel structure on combustion as demonstrated by the isomers of heptane: a rapid compression machine study, *Proceedings of the Combustion Institute* 30 (2) (2005) 2639–2647. doi:10.1016/j.proci.2004.08.180.
- [95] M. Fikri, L. Cancino, M. Hartmann, C. Schulz, High-pressure shock-tube investigation of the impact of 3-pentanone on the ignition properties of primary reference fuels, *Proceedings of the Combustion Institute* 34 (1) (2013) 393–400. doi:10.1016/j.proci.2012.05.101.
- [96] K. Fieweger, R. Blumenthal, G. Adomeit, Self-ignition of SI engine model fuels: A shock tube investigation at high pressure, *Combustion and Flame* 109 (4) (1997) 599–619. doi:10.1016/S0010-2180(97)00049-7.

- [97] K. Yong, J. He, W. Zhang, L. Xian, C. Zhang, P. Li, X. Li, Shock tube study of n-nonane/air ignition over a wide range of temperatures, *Fuel* 188 (2017) 567–574. doi:10.1016/j.fuel.2016.09.054.
- [98] U. Pfahl, K. Fieweger, G. Adomeit, Self-ignition of diesel-relevant hydrocarbon-air mixtures under engine conditions, in: *Symposium (International) on Combustion*, Vol. 26, Elsevier, 1996, pp. 781–789. doi:10.1016/S0082-0784(96)80287-6.
- [99] V. Simanzhenkov, R. Idem, *Crude oil chemistry*, CRC Press, 2003.
- [100] S. S. Vasu, D. F. Davidson, Z. Hong, V. Vasudevan, R. K. Hanson, n-dodecane oxidation at high-pressures: Measurements of ignition delay times and OH concentration time-histories, *Proceedings of the Combustion Institute* 32 (1) (2009) 173–180. doi:10.1016/j.proci.2008.05.006.
- [101] D. Healy, N. S. Donato, C. J. Aul, E. L. Petersen, C. M. Zinner, G. Bourque, H. J. Curran, Isobutane ignition delay time measurements at high pressure and detailed chemical kinetic simulations, *Combustion and Flame* 157 (8) (2010) 1540–1551. doi:10.1016/j.combustflame.2010.01.011.
- [102] K. Zhang, C. Banyon, J. Bugler, H. J. Curran, A kinetic modeling study on the oxidation of five hexane isomers, in: *Proceedings of the 7th European Combustion Meeting*, Budapest, Hungary, 2015.
- [103] R. Stone, *Introduction to internal combustion engines*, Springer, 1999. doi:10.1007/978-1-349-14916-2.
- [104] D. S. J. Jones, P. P. Pujadó, *Handbook of petroleum processing*, Springer Science & Business Media, 2006. doi:10.1007/1-4020-2820-2.
- [105] P. Leprince, *Petroleum Refining: Vol. 3: Conversion Processes*, Editions Technip, 2000.
- [106] S. Y. Mohamed, L. Cai, F. Khaled, C. Banyon, Z. Wang, M. J. Al Rashidi, H. Pitsch, H. J. Curran, A. Farooq, S. M. Sarathy, Modeling ignition of a heptane isomer: improved thermodynamics, reaction pathways, kinetics, and rate rule optimizations for 2-methylhexane, *The Journal of Physical Chemistry A* 120 (14) (2016) 2201–2217. doi:10.1021/acs.jpca.6b00907.
- [107] C. Callahan, T. Held, F. Dryer, R. Minetti, M. Ribaucour, L. Sochet, T. Faravelli, P. Gaffuri, E. Rani, Experimental data and kinetic modeling of primary reference fuel mixtures, in: *Symposium (International) on Combustion*, Vol. 26, Elsevier, 1996, pp. 739–746. doi:10.1016/S0082-0784(96)80282-7.
- [108] N. Atef, G. Kukkadapu, S. Y. Mohamed, M. Al Rashidi, C. Banyon, M. Mehl, K. A. Heufer, E. F. Nasir, A. Alfazazi, A. K. Das, C. K. Westborrk, W. J. Pitz,

- T. Lu, A. Farooq, C.-J. Sung, H. J. Curran, S. M. Sarathy, A comprehensive iso-octane combustion model with improved thermochemistry and chemical kinetics, *Combustion and Flame* 178 (2017) 111–134. doi:10.1016/j.combustflame.2016.12.029.
- [109] S. M. Burke, U. Burke, R. Mc Donagh, O. Mathieu, I. Osorio, C. Keese, A. Morones, E. L. Petersen, W. Wang, T. A. DeVerter, et al., An experimental and modeling study of propene oxidation. part 2: Ignition delay time and flame speed measurements, *Combustion and Flame* 162 (2) (2015) 296–314. doi:10.1016/j.combustflame.2014.07.032.
- [110] Y. Li, C.-W. Zhou, K. P. Somers, K. Zhang, H. J. Curran, The oxidation of 2-butene: A high pressure ignition delay, kinetic modeling study and reactivity comparison with isobutene and 1-butene, *Proceedings of the Combustion Institute* 36 (1) (2017) 403–411. doi:10.1016/j.proci.2016.05.052.
- [111] C.-W. Zhou, Y. Li, E. O'Connor, K. P. Somers, S. Thion, C. Keese, O. Mathieu, E. L. Petersen, T. A. DeVerter, M. A. Oehlschlaeger, et al., A comprehensive experimental and modeling study of isobutene oxidation, *Combustion and Flame* 167 (2016) 353–379. doi:10.1016/j.combustflame.2016.01.021.
- [112] W. L. Kubic Jr, A group contribution method for estimating cetane and octane numbers, Tech. rep., Los Alamos National Lab.(LANL), Los Alamos, NM (United States) (2016).
- [113] W. J. Pitz, C. V. Naik, T. N. Mhaoldúin, C. K. Westbrook, H. J. Curran, J. P. Orme, J. M. Simmie, Modeling and experimental investigation of methylcyclohexane ignition in a rapid compression machine, *Proceedings of the combustion institute* 31 (1) (2007) 267–275. doi:10.1016/j.proci.2006.08.041.
- [114] J. Vanderover, M. A. Oehlschlaeger, Ignition time measurements for methylcyclohexane-and ethylcyclohexane-air mixtures at elevated pressures, *International Journal of Chemical Kinetics* 41 (2) (2009) 82–91. doi:10.1002/kin.20370.
- [115] S. Vasu, N. N. Parikh, R. K. Hanson, Modeling and experimental investigation of methylcyclohexane ignition in a rapid compression machine, *Proceedings of the 5th U.S. National Combustion Meeting* (D17, 3/2007).
- [116] D. Lee, Autoignition measurements for oxygenated fuels in a rapid compression machine, Ph.D. thesis, Massachusetts Institute of Technology (1993).
- [117] S. B. Saharin, Vaporization and autoignition characteristics of ethanol and 1-propanol droplets: influence of water, Ph.D. thesis, Université de Bourgogne (2013).
URL <https://tel.archives-ouvertes.fr/tel-00909646>

- [118] C. Lee, S. Vranckx, K. A. Heufer, S. V. Khomik, Y. Uygun, H. Olivier, R. X. Fernandez, On the chemical kinetics of ethanol oxidation: shock tube, rapid compression machine and detailed modeling study, *Zeitschrift für Physikalische Chemie International journal of research in physical chemistry and chemical physics* 226 (1) (2012) 1–28. doi:10.1524/zpch.2012.0185.
- [119] S. Pischinger, M. Günther, O. Budak, Abnormal combustion phenomena with different fuels in a spark ignition engine with direct fuel injection, *Combustion and Flame* 175 (2017) 123–137. doi:10.1016/j.combustflame.2016.09.010.
- [120] E. Christensen, J. Yanowitz, M. Ratcliff, R. L. McCormick, Renewable oxygenate blending effects on gasoline properties, *Energy & Fuels* 25 (10) (2011) 4723–4733. doi:10.1021/es402793p.
- [121] B. W. Weber, K. Kumar, Y. Zhang, C.-J. Sung, Autoignition of n-butanol at elevated pressure and low-to-intermediate temperature, *Combustion and Flame* 158 (5) (2011) 809–819. doi:10.1016/j.combustflame.2011.02.005.
- [122] B. W. Weber, C.-J. Sung, Comparative autoignition trends in butanol isomers at elevated pressure, *Energy & Fuels* 27 (3) (2013) 1688–1698. doi:10.1021/ef302195c.
- [123] A. S. AlRamadan, J. Badra, T. Javed, M. Al-Abbad, N. Bokhumseen, P. Gailard, H. Babiker, A. Farooq, S. M. Sarathy, Mixed butanols addition to gasoline surrogates: Shock tube ignition delay time measurements and chemical kinetic modeling, *Combustion and Flame* 162 (10) (2015) 3971–3979. doi:10.1016/j.combustflame.2015.07.035.
- [124] T. Tsujimura, W. J. Pitz, F. Gillespie, H. J. Curran, B. W. Weber, Y. Zhang, C.-J. Sung, Development of isopentanol reaction mechanism reproducing autoignition character at high and low temperatures, *Energy & Fuels* 26 (8) (2012) 4871–4886. doi:10.1021/ef300879k.
- [125] L. Cai, Y. Uygun, C. Togbé, H. Pitsch, H. Olivier, P. Dagaut, S. M. Sarathy, An experimental and modeling study of n-octanol combustion, *Proceedings of the Combustion Institute* 35 (1) (2015) 419–427. doi:10.1016/j.proci.2014.05.088.
- [126] M. Graboski, An analysis of alternatives for unleaded petrol additives for South Africa, <http://www.unep.org/transport/pcfvp/pdf/pubgraboskireport.pdf>.
- [127] A. Brassat, M. Thewes, M. Müther, S. Pischinger, C. Lee, R. X. Fernandes, H. Olivier, Y. Uygun, Analysis of the effects of certain alcohol and furan-based biofuels on controlled auto ignition, *SAE Technical Paper* 2012-01-1135. doi:10.4271/2012-01-1135.

- [128] H. Nakamura, D. Darcy, M. Mehl, C. J. Tobin, W. K. Metcalfe, W. J. Pitz, C. K. Westbrook, H. J. Curran, An experimental and modeling study of shock tube and rapid compression machine ignition of n-butylbenzene/air mixtures, *Combustion and Flame* 161 (1) (2014) 49–64. doi:10.1016/j.combustflame.2013.08.002.
- [129] G. Kukkadapu, B. W. Weber, C.-J. Sung, Autoignition study of tetralin in a rapid compression machine at elevated pressures and low-to-intermediate temperatures, *Fuel* 159 (2015) 436–445. doi:10.1016/j.fuel.2015.06.093.
- [130] W. Cannella, M. Foster, G. Gunter, W. Leppard, FACE gasolines and blends with ethanol: detailed characterization of physical and chemical properties (2014). URL <http://www.crcao.com/reports/recentstudies2014/AVFL-24/AVFL-24%20FACE%20Gasolines%20Report%20-%20071414.pdf>
- [131] T. Javed, E. F. Nasir, A. Ahmed, J. Badra, K. Djebbi, M. Beshir, W. Ji, S. M. Sarathy, A. Farooq, Ignition delay measurements of light naphtha: A fully blended low octane fuel, *Proceedings of the Combustion Institute* 36 (1) (2017) 315–322. doi:10.1016/j.proci.2016.05.043.
- [132] M. AlAbbad, T. Javed, F. Khaled, J. Badra, A. Farooq, Ignition delay time measurements of primary reference fuel blends, *Combustion and Flame* 178 (2017) 205–216. doi:10.1016/j.combustflame.2016.12.027.
- [133] R. Di Sante, Measurements of the auto-ignition of n-heptane/toluene mixtures using a rapid compression machine, *Combustion and flame* 159 (1) (2012) 55–63. doi:10.1016/j.combustflame.2011.05.020.
- [134] J. Herzler, M. Fikri, K. Hitzbleck, R. Starke, C. Schulz, P. Roth, G. T. Kalghatgi, Shock-tube study of the autoignition of n-heptane/toluene/air mixtures at intermediate temperatures and high pressures, *Combustion and flame* 149 (1) (2007) 25–31. doi:10.1016/j.combustflame.2006.12.015.
- [135] M. Fikri, J. Herzler, R. Starke, C. Schulz, P. Roth, G. T. Kalghatgi, Autoignition of gasoline surrogates mixtures at intermediate temperatures and high pressures, *Combustion and flame* 152 (1) (2008) 276–281. doi:10.1016/j.combustflame.2007.07.010.
- [136] L. Cancino, M. Fikri, A. Oliveira, C. Schulz, Autoignition of gasoline surrogate mixtures at intermediate temperatures and high pressures: Experimental and numerical approaches, *Proceedings of the Combustion Institute* 32 (1) (2009) 501–508. doi:10.1016/j.proci.2008.06.180.
- [137] G. T. Kalghatgi, The outlook for fuels for internal combustion engines, *International Journal of Engine Research* 15 (4) (2014) 383–398. doi:10.1177/1468087414526189.

- [138] T. Javed, Combustion kinetic studies of gasolines and surrogates, Ph.D. thesis, King Abdullah University of Science and Technology (2016).
URL <http://hdl.handle.net/10754/621837>
- [139] E. O. Lebigot, Uncertainties: A python package for calculations with uncertainties (2016).
URL <https://pypi.python.org/pypi/uncertainties/>
- [140] X. He, M. Donovan, B. Zigler, T. Palmer, S. Walton, M. Wooldridge, A. Atreya, An experimental and modeling study of iso-octane ignition delay times under homogeneous charge compression ignition conditions, *Combustion and Flame* 142 (3) (2005) 266–275. doi:10.1016/j.combustflame.2005.02.014.
- [141] B. Gauthier, D. F. Davidson, R. K. Hanson, Shock tube determination of ignition delay times in full-blend and surrogate fuel mixtures, *Combustion and Flame* 139 (4) (2004) 300–311. doi:10.1016/j.combustflame.2004.08.015.

SUPPLEMENTARY MATERIAL

Table S1: Fuel matrix of PRF

Fuel	Volume fraction		Mole fraction		RON ¹	MON ¹
	<i>iso</i> -Octane	<i>n</i> -Heptane	<i>iso</i> -Octane	<i>n</i> -Heptane		
PRF 0	0.000	1.000	0.000	1.000	0.0	0.0
PRF 5	0.050	0.950	0.045	0.955	5.0	5.0
PRF 10	0.100	0.900	0.090	0.910	10.0	10.0
PRF 15	0.150	0.850	0.135	0.865	15.0	15.0
PRF 20	0.200	0.800	0.182	0.818	20.0	20.0
PRF 25	0.250	0.750	0.228	0.772	25.0	25.0
PRF 30	0.300	0.700	0.276	0.724	30.0	30.0
PRF 35	0.350	0.650	0.323	0.677	35.0	35.0
PRF 40	0.400	0.600	0.372	0.628	40.0	40.0
PRF 45	0.450	0.550	0.421	0.579	45.0	45.0
PRF 50	0.500	0.500	0.470	0.530	50.0	50.0
PRF 55	0.550	0.450	0.520	0.480	55.0	55.0
PRF 60	0.600	0.400	0.571	0.429	60.0	60.0
PRF 65	0.650	0.350	0.622	0.378	65.0	65.0
PRF 70	0.700	0.300	0.674	0.326	70.0	70.0
PRF 75	0.750	0.250	0.727	0.273	75.0	75.0
PRF 80	0.800	0.200	0.780	0.220	80.0	80.0
PRF 85	0.850	0.150	0.834	0.166	85.0	85.0
PRF 90	0.900	0.100	0.889	0.111	90.0	90.0
PRF 95	0.950	0.050	0.944	0.056	95.0	95.0
PRF 100	1.000	0.000	1.000	0.000	100.0	100.0

¹ ASTM D2699, D2700 [3, 4]

Table S2: Fuel matrix of TRF

Fuel	Volume fraction		Mole fraction		RON	MON
	Toluene	<i>n</i> -Heptane	Toluene	<i>n</i> -Heptane		
TRF 5	0.050	0.950	0.067	0.933	5.9 ¹	5.0 ¹
TRF 10	0.100	0.900	0.132	0.868	13.4 ¹	11.6 ¹
TRF 15	0.150	0.850	0.195	0.805	20.7 ¹	18.0 ¹
TRF 20	0.200	0.800	0.256	0.744	27.7 ¹	24.2 ¹
TRF 25	0.250	0.750	0.314	0.686	34.5 ¹	30.2 ¹
TRF 30	0.300	0.700	0.371	0.629	41.1 ¹	36.0 ¹
TRF 35	0.350	0.650	0.425	0.575	47.5 ¹	41.6 ¹
TRF 40	0.400	0.600	0.478	0.522	53.7 ¹	47.1 ¹
TRF 45	0.450	0.550	0.529	0.471	59.7 ¹	52.4 ¹
TRF 50	0.500	0.500	0.579	0.421	65.1 ²	58.0 ²
TRF 55	0.550	0.450	0.627	0.373	71.3 ¹	62.6 ¹
TRF 60	0.600	0.400	0.673	0.327	77.9 ²	68.5 ²
TRF 65	0.650	0.350	0.718	0.282	84.5 ²	74.5 ²
TRF 70	0.700	0.300	0.762	0.238	89.3 ²	78.2 ²
TRF 75	0.750	0.250	0.805	0.195	94.2 ²	82.6 ²
TRF 80	0.800	0.200	0.846	0.154	97.6 ¹	85.8 ¹
TRF 85	0.850	0.150	0.886	0.114	102.3 ²	91.6 ²
TRF 90	0.900	0.100	0.925	0.075	107.2 ¹	94.2 ¹
TRF 95	0.950	0.050	0.963	0.037	111.8 ¹	98.3 ¹
TRF 100	1.000	0.000	1.000	0.000	116.3 ¹	102.2 ¹

¹ Blending rule in [30]² ASTM D2699, D2700 measurements [3, 4] in [33]

Table S3: Fuel matrix of TPRF

Fuel	Volume fraction			Mole fraction			RON ¹	MON ¹
	Toluene	<i>iso</i> -octane	<i>n</i> -heptane	Toluene	<i>iso</i> -octane	<i>n</i> -heptane		
TPRF 5-5	0.050	0.050	0.900	0.068	0.044	0.888	10.9	10.0
TPRF 5-10	0.050	0.100	0.850	0.068	0.088	0.844	15.9	14.9
TPRF 5-15	0.050	0.150	0.800	0.069	0.133	0.799	20.8	19.9
TPRF 5-20	0.050	0.200	0.750	0.069	0.178	0.753	25.8	24.9
TPRF 5-25	0.050	0.250	0.700	0.069	0.224	0.707	30.8	29.8
TPRF 5-30	0.050	0.300	0.650	0.070	0.270	0.660	35.7	34.7
TPRF 5-35	0.050	0.350	0.600	0.070	0.317	0.613	40.6	39.7
TPRF 5-40	0.050	0.400	0.550	0.071	0.365	0.565	45.6	44.6
TPRF 5-45	0.050	0.450	0.500	0.071	0.413	0.516	50.5	49.5
TPRF 5-50	0.050	0.500	0.450	0.071	0.461	0.468	55.5	54.5
TPRF 5-55	0.050	0.550	0.400	0.072	0.510	0.418	60.4	59.4
TPRF 5-60	0.050	0.600	0.350	0.072	0.560	0.368	65.3	64.3

Table S3: (continued) Fuel matrix of TPRF

Fuel	Volume fraction			Mole fraction			RON ¹	MON ¹
	Toluene	<i>iso</i> -Octane	<i>n</i> -Heptane	Toluene	<i>iso</i> -Octane	<i>n</i> -Heptane		
TPRF 5-65	0.050	0.650	0.300	0.073	0.610	0.317	70.2	69.2
TPRF 5-70	0.050	0.700	0.250	0.073	0.661	0.266	75.1	74.1
TPRF 5-75	0.050	0.750	0.200	0.074	0.712	0.214	80.0	79.0
TPRF 5-80	0.050	0.800	0.150	0.074	0.765	0.162	84.9	83.9
TPRF 5-85	0.050	0.850	0.100	0.074	0.817	0.108	89.8	88.7
TPRF 5-90	0.050	0.900	0.050	0.075	0.871	0.054	94.7	93.6
TPRF 5-95	0.050	0.950	0.000	0.075	0.925	0.000	99.6	98.5
TPRF 10-5	0.100	0.050	0.850	0.133	0.043	0.824	18.3	16.5
TPRF 10-10	0.100	0.100	0.800	0.134	0.086	0.780	23.3	21.4
TPRF 10-15	0.100	0.150	0.750	0.135	0.130	0.735	28.2	26.3
TPRF 10-20	0.100	0.200	0.700	0.135	0.175	0.690	33.1	31.2
TPRF 10-25	0.100	0.250	0.650	0.136	0.220	0.644	38.0	36.1
TPRF 10-30	0.100	0.300	0.600	0.137	0.265	0.598	42.9	41.0
TPRF 10-35	0.100	0.350	0.550	0.138	0.311	0.551	47.7	45.8
TPRF 10-40	0.100	0.400	0.500	0.138	0.358	0.504	52.6	50.7
TPRF 10-45	0.100	0.450	0.450	0.139	0.405	0.456	57.4	55.5
TPRF 10-50	0.100	0.500	0.400	0.140	0.452	0.408	62.3	60.3
TPRF 10-55	0.100	0.550	0.350	0.141	0.500	0.359	67.1	65.2
TPRF 10-60	0.100	0.600	0.300	0.142	0.549	0.309	71.9	70.0
TPRF 10-65	0.100	0.650	0.250	0.142	0.598	0.259	76.7	74.7
TPRF 10-70	0.100	0.700	0.200	0.143	0.648	0.209	81.5	79.5
TPRF 10-75	0.100	0.750	0.150	0.144	0.698	0.157	86.3	84.3
TPRF 10-80	0.100	0.800	0.100	0.145	0.749	0.106	91.1	89.1
TPRF 10-85	0.100	0.850	0.050	0.146	0.801	0.053	95.8	93.8
TPRF 10-90	0.100	0.900	0.000	0.147	0.853	0.000	100.6	98.5
TPRF 15-5	0.150	0.050	0.800	0.196	0.042	0.762	25.5	22.9
TPRF 15-10	0.150	0.100	0.750	0.197	0.085	0.718	30.4	27.7
TPRF 15-15	0.150	0.150	0.700	0.198	0.128	0.674	35.3	32.5
TPRF 15-20	0.150	0.200	0.650	0.199	0.172	0.629	40.1	37.4
TPRF 15-25	0.150	0.250	0.600	0.200	0.216	0.584	44.9	42.2
TPRF 15-30	0.150	0.300	0.550	0.202	0.260	0.538	49.8	47.0
TPRF 15-35	0.150	0.350	0.500	0.203	0.306	0.492	54.6	51.7
TPRF 15-40	0.150	0.400	0.450	0.204	0.351	0.445	59.3	56.5
TPRF 15-45	0.150	0.450	0.400	0.205	0.397	0.398	64.1	61.2
TPRF 15-50	0.150	0.500	0.350	0.206	0.444	0.350	68.8	66.0
TPRF 15-55	0.150	0.550	0.300	0.207	0.491	0.302	73.6	70.7
TPRF 15-60	0.150	0.600	0.250	0.208	0.539	0.253	78.3	75.4
TPRF 15-65	0.150	0.650	0.200	0.210	0.587	0.203	83.0	80.1
TPRF 15-70	0.150	0.700	0.150	0.211	0.636	0.153	87.7	84.7
TPRF 15-75	0.150	0.750	0.100	0.212	0.685	0.103	92.3	89.3
TPRF 15-80	0.150	0.800	0.050	0.213	0.735	0.052	97.0	94.0
TPRF 15-85	0.150	0.850	0.000	0.215	0.785	0.000	101.6	98.6
TPRF 20-5	0.200	0.050	0.750	0.257	0.042	0.702	32.5	29.0
TPRF 20-10	0.200	0.100	0.700	0.258	0.083	0.658	37.3	33.8
TPRF 20-15	0.200	0.150	0.650	0.260	0.126	0.614	42.1	38.6
TPRF 20-20	0.200	0.200	0.600	0.261	0.169	0.570	46.9	43.3
TPRF 20-25	0.200	0.250	0.550	0.263	0.212	0.525	51.7	48.0
TPRF 20-30	0.200	0.300	0.500	0.264	0.256	0.480	56.4	52.8
TPRF 20-35	0.200	0.350	0.450	0.265	0.300	0.435	61.1	57.4

Table S3: (continued) Fuel matrix of TPRF

Fuel	Volume fraction			Mole fraction			RON ¹	MON ¹
	Toluene	<i>iso</i> -Octane	<i>n</i> -Heptane	Toluene	<i>iso</i> -Octane	<i>n</i> -Heptane		
TPRF 20-40	0.200	0.400	0.400	0.267	0.345	0.388	65.8	62.1
TPRF 20-45	0.200	0.450	0.350	0.268	0.390	0.342	70.5	66.8
TPRF 20-50	0.200	0.500	0.300	0.270	0.436	0.295	75.1	71.4
TPRF 20-55	0.200	0.550	0.250	0.271	0.482	0.247	79.8	76.0
TPRF 20-60	0.200	0.600	0.200	0.273	0.529	0.199	84.4	80.6
TPRF 20-65	0.200	0.650	0.150	0.274	0.576	0.150	88.9	85.1
TPRF 20-70	0.200	0.700	0.100	0.276	0.624	0.100	93.5	89.6
TPRF 20-75	0.200	0.750	0.050	0.277	0.672	0.050	98.0	94.1
TPRF 20-80	0.200	0.800	0.000	0.279	0.721	0.000	102.5	98.6
TPRF 25-5	0.250	0.050	0.700	0.316	0.041	0.643	39.3	34.9
TPRF 25-10	0.250	0.100	0.650	0.317	0.082	0.601	44.0	39.7
TPRF 25-15	0.250	0.150	0.600	0.319	0.124	0.557	48.8	44.4
TPRF 25-20	0.250	0.200	0.550	0.321	0.166	0.514	53.5	49.0
TPRF 25-25	0.250	0.250	0.500	0.322	0.208	0.469	58.2	53.7
TPRF 25-30	0.250	0.300	0.450	0.324	0.251	0.425	62.8	58.3
TPRF 25-35	0.250	0.350	0.400	0.326	0.295	0.379	67.5	62.9
TPRF 25-40	0.250	0.400	0.350	0.328	0.339	0.334	72.1	67.5
TPRF 25-45	0.250	0.450	0.300	0.329	0.383	0.288	76.6	72.0
TPRF 25-50	0.250	0.500	0.250	0.331	0.428	0.241	81.2	76.6
TPRF 25-55	0.250	0.550	0.200	0.333	0.473	0.194	85.7	81.0
TPRF 25-60	0.250	0.600	0.150	0.335	0.519	0.146	90.2	85.5
TPRF 25-65	0.250	0.650	0.100	0.337	0.565	0.098	94.6	89.9
TPRF 25-70	0.250	0.700	0.050	0.338	0.612	0.049	99.0	94.3
TPRF 25-75	0.250	0.750	0.000	0.340	0.660	0.000	103.4	98.6
TPRF 30-5	0.300	0.050	0.650	0.372	0.040	0.587	45.8	40.7
TPRF 30-10	0.300	0.100	0.600	0.374	0.081	0.545	50.5	45.4
TPRF 30-15	0.300	0.150	0.550	0.376	0.122	0.502	55.2	50.0
TPRF 30-20	0.300	0.200	0.500	0.378	0.163	0.459	59.8	54.6
TPRF 30-25	0.300	0.250	0.450	0.380	0.205	0.415	64.5	59.2
TPRF 30-30	0.300	0.300	0.400	0.382	0.247	0.371	69.0	63.7
TPRF 30-35	0.300	0.350	0.350	0.384	0.290	0.326	73.6	68.2
TPRF 30-40	0.300	0.400	0.300	0.386	0.333	0.281	78.1	72.7
TPRF 30-45	0.300	0.450	0.250	0.388	0.376	0.236	82.5	77.1
TPRF 30-50	0.300	0.500	0.200	0.390	0.420	0.189	87.0	81.5
TPRF 30-55	0.300	0.550	0.150	0.392	0.465	0.143	91.3	85.8
TPRF 30-60	0.300	0.600	0.100	0.395	0.510	0.096	95.7	90.1
TPRF 30-65	0.300	0.650	0.050	0.397	0.555	0.048	100.0	94.4
TPRF 30-70	0.300	0.700	0.000	0.399	0.601	0.000	104.3	98.6
TPRF 35-5	0.350	0.050	0.600	0.427	0.039	0.533	52.2	46.3
TPRF 35-10	0.350	0.100	0.550	0.429	0.079	0.491	56.8	50.9
TPRF 35-15	0.350	0.150	0.500	0.432	0.120	0.449	61.4	55.4
TPRF 35-20	0.350	0.200	0.450	0.434	0.160	0.406	66.0	60.0
TPRF 35-25	0.350	0.250	0.400	0.436	0.201	0.363	70.5	64.4
TPRF 35-30	0.350	0.300	0.350	0.438	0.243	0.319	75.0	68.9
TPRF 35-35	0.350	0.350	0.300	0.441	0.285	0.275	79.4	73.3
TPRF 35-40	0.350	0.400	0.250	0.443	0.327	0.230	83.8	77.6
TPRF 35-45	0.350	0.450	0.200	0.445	0.370	0.185	88.2	81.9
TPRF 35-50	0.350	0.500	0.150	0.447	0.413	0.140	92.5	86.2
TPRF 35-55	0.350	0.550	0.100	0.450	0.457	0.094	96.7	90.4

Table S3: (continued) Fuel matrix of TPRF

Fuel	Volume fraction			Mole fraction			RON ¹	MON ¹
	Toluene	<i>iso</i> -Octane	<i>n</i> -Heptane	Toluene	<i>iso</i> -Octane	<i>n</i> -Heptane		
TPRF 35-60	0.350	0.600	0.050	0.452	0.501	0.047	100.9	94.6
TPRF 35-65	0.350	0.650	0.000	0.455	0.545	0.000	105.1	98.7
TPRF 40-5	0.400	0.050	0.550	0.480	0.039	0.481	58.3	51.7
TPRF 40-10	0.400	0.100	0.500	0.483	0.078	0.439	62.9	56.2
TPRF 40-15	0.400	0.150	0.450	0.485	0.118	0.397	67.4	60.7
TPRF 40-20	0.400	0.200	0.400	0.488	0.157	0.355	71.9	65.1
TPRF 40-25	0.400	0.250	0.350	0.490	0.198	0.312	76.4	69.5
TPRF 40-30	0.400	0.300	0.300	0.492	0.239	0.269	80.7	73.9
TPRF 40-35	0.400	0.350	0.250	0.495	0.280	0.225	85.1	78.1
TPRF 40-40	0.400	0.400	0.200	0.498	0.321	0.181	89.3	82.4
TPRF 40-45	0.400	0.450	0.150	0.500	0.363	0.136	93.5	86.5
TPRF 40-50	0.400	0.500	0.100	0.503	0.406	0.091	97.7	90.6
TPRF 40-55	0.400	0.550	0.050	0.505	0.449	0.046	101.8	94.7
TPRF 40-60	0.400	0.600	0.000	0.508	0.492	0.000	105.9	98.7
TPRF 45-5	0.450	0.050	0.500	0.532	0.038	0.430	64.3	56.9
TPRF 45-10	0.450	0.100	0.450	0.534	0.077	0.389	68.8	61.4
TPRF 45-15	0.450	0.150	0.400	0.537	0.116	0.347	73.3	65.8
TPRF 45-20	0.450	0.200	0.350	0.540	0.155	0.305	77.7	70.1
TPRF 45-25	0.450	0.250	0.300	0.542	0.195	0.263	82.0	74.4
TPRF 45-30	0.450	0.300	0.250	0.545	0.235	0.220	86.2	78.6
TPRF 45-35	0.450	0.350	0.200	0.548	0.275	0.177	90.4	82.8
TPRF 45-40	0.450	0.400	0.150	0.550	0.316	0.134	94.6	86.9
TPRF 45-45	0.450	0.450	0.100	0.553	0.357	0.089	98.7	90.9
TPRF 45-50	0.450	0.500	0.050	0.556	0.399	0.045	102.7	94.8
TPRF 45-55	0.450	0.550	0.000	0.559	0.441	0.000	106.6	98.7
TPRF 50-5	0.500	0.050	0.450	0.581	0.038	0.381	70.1	62.0
TPRF 50-10	0.500	0.100	0.400	0.584	0.075	0.340	74.5	66.4
TPRF 50-15	0.500	0.150	0.350	0.587	0.114	0.299	78.9	70.7
TPRF 50-20	0.500	0.200	0.300	0.590	0.152	0.258	83.2	74.9
TPRF 50-25	0.500	0.250	0.250	0.593	0.191	0.216	87.4	79.1
TPRF 50-30	0.500	0.300	0.200	0.596	0.231	0.173	91.5	83.2
TPRF 50-35	0.500	0.350	0.150	0.599	0.271	0.131	95.6	87.2
TPRF 50-40	0.500	0.400	0.100	0.602	0.311	0.088	99.6	91.1
TPRF 50-45	0.500	0.450	0.050	0.605	0.351	0.044	103.5	95.0
TPRF 50-50	0.500	0.500	0.000	0.608	0.392	0.000	107.3	98.7
TPRF 55-5	0.550	0.050	0.400	0.630	0.037	0.333	75.7	67.0
TPRF 55-10	0.550	0.100	0.350	0.633	0.074	0.293	80.1	71.3
TPRF 55-15	0.550	0.150	0.300	0.636	0.112	0.252	84.3	75.5
TPRF 55-20	0.550	0.200	0.250	0.639	0.150	0.211	88.5	79.6
TPRF 55-25	0.550	0.250	0.200	0.642	0.188	0.170	92.6	83.6
TPRF 55-30	0.550	0.300	0.150	0.645	0.227	0.128	96.6	87.5
TPRF 55-35	0.550	0.350	0.100	0.648	0.266	0.086	100.5	91.4
TPRF 55-40	0.550	0.400	0.050	0.651	0.306	0.043	104.3	95.1
TPRF 55-45	0.550	0.450	0.000	0.654	0.346	0.000	108.0	98.8
TPRF 60-5	0.600	0.050	0.350	0.676	0.036	0.287	81.2	71.8
TPRF 60-10	0.600	0.100	0.300	0.680	0.073	0.247	85.4	75.9
TPRF 60-15	0.600	0.150	0.250	0.683	0.110	0.207	89.6	80.0
TPRF 60-20	0.600	0.200	0.200	0.686	0.148	0.166	93.6	84.0

Table S3: (continued) Fuel matrix of TPRF

Fuel	Volume fraction			Mole fraction			RON ¹	MON ¹
	Toluene	<i>iso</i> -Octane	<i>n</i> -Heptane	Toluene	<i>iso</i> -Octane	<i>n</i> -Heptane		
TPRF 60-25	0.600	0.250	0.150	0.689	0.185	0.125	97.5	87.9
TPRF 60-30	0.600	0.300	0.100	0.692	0.224	0.084	101.3	91.6
TPRF 60-35	0.600	0.350	0.050	0.696	0.262	0.042	105.0	95.3
TPRF 60-40	0.600	0.400	0.000	0.699	0.301	0.000	108.6	98.8
TPRF 65-5	0.650	0.050	0.300	0.722	0.036	0.242	86.5	76.4
TPRF 65-10	0.650	0.100	0.250	0.725	0.072	0.203	90.6	80.5
TPRF 65-15	0.650	0.150	0.200	0.728	0.109	0.163	94.6	84.4
TPRF 65-20	0.650	0.200	0.150	0.732	0.145	0.123	98.4	88.2
TPRF 65-25	0.650	0.250	0.100	0.735	0.183	0.082	102.2	91.9
TPRF 65-30	0.650	0.300	0.050	0.738	0.220	0.041	105.8	95.4
TPRF 65-35	0.650	0.350	0.000	0.742	0.258	0.000	109.3	98.8
TPRF 70-5	0.700	0.050	0.250	0.766	0.035	0.199	91.6	80.9
TPRF 70-10	0.700	0.100	0.200	0.769	0.071	0.160	95.6	84.8
TPRF 70-15	0.700	0.150	0.150	0.773	0.107	0.121	99.4	88.6
TPRF 70-20	0.700	0.200	0.100	0.776	0.143	0.081	103.0	92.1
TPRF 70-25	0.700	0.250	0.050	0.780	0.180	0.041	106.5	95.6
TPRF 70-30	0.700	0.300	0.000	0.783	0.217	0.000	109.8	98.8
TPRF 75-5	0.750	0.050	0.200	0.808	0.035	0.157	96.6	85.3
TPRF 75-10	0.750	0.100	0.150	0.812	0.070	0.118	100.3	88.9
TPRF 75-15	0.750	0.150	0.100	0.815	0.105	0.079	103.9	92.4
TPRF 75-20	0.750	0.200	0.050	0.819	0.141	0.040	107.3	95.7
TPRF 75-25	0.750	0.250	0.000	0.823	0.177	0.000	110.4	98.8
TPRF 80-5	0.800	0.050	0.150	0.850	0.034	0.116	101.3	89.4
TPRF 80-10	0.800	0.100	0.100	0.853	0.069	0.078	104.8	92.8
TPRF 80-15	0.800	0.150	0.050	0.857	0.104	0.039	108.0	96.0
TPRF 80-20	0.800	0.200	0.000	0.861	0.139	0.000	111.0	98.9
TPRF 85-5	0.850	0.050	0.100	0.890	0.034	0.076	105.8	93.3
TPRF 85-10	0.850	0.100	0.050	0.894	0.068	0.038	108.8	96.3
TPRF 85-15	0.850	0.150	0.000	0.898	0.102	0.000	111.5	98.9
TPRF 90-5	0.900	0.050	0.050	0.929	0.033	0.038	109.9	96.8
TPRF 90-10	0.900	0.100	0.000	0.933	0.067	0.000	112.0	98.9
TPRF 95-5	0.950	0.050	0.000	0.967	0.033	0.000	112.5	98.9

¹ Blending rule in [30]

Table S4: Fuel matrix of ERF

Fuel	Volume fraction		Mole fraction		RON	MON
	Ethanol	<i>n</i> -Heptane	Ethanol	<i>n</i> -Heptane		
ERF 5	0.050	0.950	0.385	0.615	12.6 ¹	10.6 ¹
ERF 10	0.100	0.900	0.455	0.545	23.5 ¹	19.8 ¹
ERF 15	0.150	0.850	0.518	0.482	33.1 ¹	27.8 ¹
ERF 20	0.200	0.800	0.575	0.425	41.6 ¹	35.0 ¹
ERF 25	0.250	0.750	0.626	0.374	49.2 ¹	41.3 ¹
ERF 30	0.300	0.700	0.672	0.328	54.3 ²	47.6 ¹
ERF 35	0.350	0.650	0.715	0.285	62.1 ¹	57.2 ¹
ERF 40	0.400	0.600	0.754	0.246	69.7 ²	64.5 ²
ERF 45	0.450	0.550	0.790	0.210	75.1 ¹	71.0 ¹
ERF 50	0.500	0.500	0.823	0.177	83.8 ²	75.9 ¹
ERF 55	0.550	0.450	0.854	0.146	88.9 ¹	79.8 ¹
ERF 60	0.600	0.400	0.883	0.117	94.7 ²	83.8 ²
ERF 65	0.650	0.350	0.909	0.091	97.7 ¹	85.2 ¹
ERF 70	0.700	0.300	0.934	0.066	101.6 ²	87.0 ¹
ERF 75	0.750	0.250	0.958	0.042	103.1 ¹	88.4 ¹
ERF 80	0.800	0.200	0.979	0.021	104.7 ²	88.9 ²
ERF 85	0.850	0.150	1.000	0.000	106.2 ¹	90.0 ¹
ERF 90	0.900	0.100	0.391	0.499	106.5 ²	90.5 ¹
ERF 95	0.950	0.050	0.524	0.390	107.7 ¹	90.7 ¹
ERF 100	1.000	0.000	0.631	0.302	109.0 ³	90.0 ³

¹ Blending rule in [31]² ASTM D2699, D2700 measurements [3, 4] in [34]³ ASTM D2699, D2700 measurements [3, 4] in [64]

Table S5: Fuel matrix of EPRF

Fuel	Volume percentage			Mole fraction			RON	MON
	Ethanol	<i>iso</i> -Octane	<i>n</i> -heptane	Ethanol	<i>iso</i> -Octane	<i>n</i> -Heptane		
EPRF 5-85.5	0.050	0.855	0.095	0.128	0.775	0.097	94.1 ²	90.4 ¹
EPRF 10-90	0.100	0.900	0.000	0.239	0.761	0.000	106.8 ²	99.9 ²
EPRF 10-81	0.100	0.810	0.090	0.237	0.678	0.085	97.6 ²	92.1 ¹
EPRF 10-72	0.100	0.720	0.180	0.235	0.597	0.168	89.5 ²	85.3 ¹
EPRF 10-54	0.100	0.540	0.360	0.230	0.440	0.330	72.8 ⁴	70.0 ⁴
EPRF 10-45	0.100	0.450	0.450	0.228	0.363	0.409	64.5 ⁴	61.0 ⁴
EPRF 10-36	0.100	0.360	0.540	0.226	0.288	0.486	55.6 ⁴	53.0 ⁴
EPRF 20-80	0.200	0.800	0.000	0.414	0.586	0.000	109.4 ²	99.1 ²
EPRF 20-72	0.200	0.720	0.080	0.411	0.523	0.066	103.6 ²	93.8 ¹
EPRF 20-64	0.200	0.640	0.160	0.408	0.462	0.130	97.0 ²	89.5 ¹
EPRF 20-48	0.200	0.480	0.320	0.402	0.341	0.256	83.4 ⁴	79.3 ⁴
EPRF 20-40	0.200	0.400	0.400	0.399	0.282	0.318	76.7 ⁴	73.0 ⁴
EPRF 20-32	0.200	0.320	0.480	0.396	0.224	0.379	69.0 ⁴	64.0 ⁴
EPRF 20-16	0.200	0.160	0.640	0.391	0.111	0.499	53.3 ²	46.5 ¹
EPRF 30-70	0.300	0.700	0.000	0.548	0.452	0.000	109.8 ¹	97.0 ¹
EPRF 30-56	0.300	0.560	0.140	0.542	0.358	0.101	101.3 ¹	91.5 ¹
EPRF 30-42	0.300	0.420	0.280	0.536	0.265	0.199	91.9 ⁴	86.0 ⁴
EPRF 30-42	0.300	0.420	0.280	0.536	0.265	0.199	91.9 ⁴	86.0 ⁴
EPRF 30-35	0.300	0.350	0.350	0.533	0.220	0.248	86.7 ⁴	81.0 ⁴
EPRF 30-28	0.300	0.280	0.420	0.530	0.175	0.296	80.7 ⁴	76.0 ⁴
EPRF 30-14	0.300	0.140	0.560	0.524	0.086	0.390	67.4 ²	57.1 ¹
EPRF 40-60	0.400	0.600	0.000	0.653	0.347	0.000	110.2 ²	95.9 ²
EPRF 40-48	0.400	0.480	0.120	0.648	0.275	0.077	105.7 ²	92.4 ¹
EPRF 40-36	0.400	0.360	0.240	0.642	0.204	0.154	98.8 ⁴	89.1 ⁴
EPRF 40-30	0.400	0.300	0.300	0.639	0.170	0.191	94.9 ⁴	86.7 ⁴
EPRF 40-24	0.400	0.240	0.360	0.637	0.135	0.228	90.5 ⁴	83.6 ⁴
EPRF 40-24	0.400	0.240	0.360	0.637	0.135	0.228	90.5 ⁴	83.6 ⁴
EPRF 40-12	0.400	0.120	0.480	0.631	0.067	0.302	80.7 ²	72.4 ¹
EPRF 50-50	0.500	0.500	0.000	0.739	0.261	0.000	109.6 ¹	94.9 ¹
EPRF 50-40	0.500	0.400	0.100	0.734	0.208	0.058	106.7 ¹	92.6 ¹
EPRF 50-30	0.500	0.300	0.200	0.729	0.155	0.116	103.0 ⁴	90.4 ⁴
EPRF 50-25	0.500	0.250	0.250	0.727	0.129	0.145	100.7 ⁴	88.8 ⁴
EPRF 50-20	0.500	0.200	0.300	0.724	0.102	0.173	97.9 ⁴	87.5 ⁴
EPRF 50-10	0.500	0.100	0.400	0.720	0.051	0.229	91.5 ²	81.6 ¹
EPRF 60-40	0.600	0.400	0.000	0.809	0.191	0.000	109.6 ²	94.2 ²
EPRF 60-32	0.600	0.320	0.080	0.805	0.152	0.043	107.7 ²	92.5 ¹
EPRF 60-24	0.600	0.240	0.160	0.801	0.113	0.085	105.0 ⁴	91.2 ⁴
EPRF 60-20	0.600	0.200	0.200	0.800	0.094	0.106	104.0 ⁴	90.2 ⁴
EPRF 60-16	0.600	0.160	0.240	0.798	0.075	0.127	102.5 ⁴	89.0 ⁴
EPRF 60-8	0.600	0.080	0.320	0.794	0.037	0.169	99.1 ²	86.9 ¹
EPRF 70-30	0.700	0.300	0.000	0.868	0.132	0.000	109.6 ¹	93.0 ¹
EPRF 70-24	0.700	0.240	0.060	0.865	0.105	0.030	107.9 ¹	92.2 ¹
EPRF 70-18	0.700	0.180	0.120	0.863	0.078	0.059	107.0 ⁴	91.0 ⁴
EPRF 70-15	0.700	0.150	0.150	0.861	0.065	0.074	105.6 ⁴	91.5 ⁴
EPRF 70-12	0.700	0.120	0.180	0.860	0.052	0.088	104.8 ⁴	89.8 ⁴
EPRF 70-6	0.700	0.060	0.240	0.857	0.026	0.117	102.7 ¹	89.8 ¹
EPRF 80-20	0.800	0.200	0.000	0.919	0.081	0.000	109.0 ²	92.6 ²

Table S5: (continued) Fuel matrix of EPRF

Fuel	Volume percentage			Mole fraction			RON	MON
	Ethanol	<i>iso</i> -Octane	<i>n</i> -Heptane	Ethanol	<i>iso</i> -Octane	<i>n</i> -Heptane		
EPRF 80-16	0.800	0.160	0.040	0.917	0.065	0.018	108.3 ²	91.7 ¹
EPRF 80-12	0.800	0.120	0.080	0.915	0.049	0.036	108.0 ⁴	91.0 ⁴
EPRF 80-10	0.800	0.100	0.100	0.914	0.040	0.046	107.0 ⁴	90.4 ⁴
EPRF 80-8	0.800	0.080	0.120	0.913	0.032	0.055	105.3 ⁴	90.2 ⁴
EPRF 80-4	0.800	0.040	0.160	0.911	0.016	0.073	105.8 ²	91.1 ¹
EPRF 90-10	0.900	0.100	0.000	0.962	0.038	0.000	108.8 ¹	91.4 ¹
EPRF 90-8	0.900	0.080	0.020	0.961	0.030	0.009	108.7 ²	91.2 ¹
EPRF 90-6	0.900	0.060	0.040	0.960	0.023	0.017	109.0 ⁴	91.6 ⁴
EPRF 90-5	0.900	0.050	0.050	0.960	0.019	0.021	108.0 ⁴	90.4 ⁴
EPRF 90-4	0.900	0.040	0.060	0.959	0.015	0.025	108.5 ⁴	91.0 ⁴
EPRF 90-2	0.900	0.020	0.080	0.959	0.008	0.034	107.2 ¹	91.3 ¹

¹ Blending rule in [31]² ASTM D2699, D2700 measurements [3, 4] in [34]³ ASTM D2699, D2700 measurements [3, 4] in [64]⁴ ASTM D2699, D2700 measurements [3, 4] in [31]

Table S6: Fuel matrix of ETPRF

Fuel	Volume percentage				Mole fraction				RON	MON
	Ethanol	Toluene	<i>iso</i> -Octane	<i>n</i> -Heptane	Ethanol	Toluene	<i>iso</i> -Octane	<i>n</i> -heptane		
ETPRF 10-9-43	0.100	0.092	0.426	0.383	0.220	0.111	0.332	0.337	71.9 ¹	68.0 ¹
ETPRF 10-10-42	0.100	0.100	0.421	0.379	0.220	0.120	0.327	0.332	71.5 ²	68.9 ²
ETPRF 10-14-65	0.100	0.135	0.653	0.112	0.222	0.164	0.514	0.099	97.8 ³	91.7 ³
ETPRF 10-18-30	0.100	0.178	0.304	0.419	0.212	0.207	0.228	0.353	70.3 ¹	65.0 ¹
ETPRF 10-20-29	0.100	0.200	0.295	0.405	0.210	0.230	0.219	0.340	71.4 ²	67.6 ²
ETPRF 10-27-48	0.100	0.268	0.479	0.153	0.210	0.308	0.355	0.128	97.0 ³	89.4 ³
ETPRF 10-36-5	0.100	0.362	0.050	0.488	0.196	0.388	0.035	0.381	68.7 ¹	59.4 ¹
ETPRF 10-40-5	0.100	0.400	0.047	0.453	0.194	0.424	0.032	0.350	71.5 ²	65.6 ²
ETPRF 10-41-31	0.100	0.405	0.312	0.183	0.198	0.439	0.219	0.144	96.0 ³	87.2 ³
ETPRF 20-8-38	0.200	0.082	0.378	0.341	0.389	0.087	0.260	0.264	82.5 ¹	77.7 ¹
ETPRF 20-10-37	0.200	0.100	0.368	0.332	0.387	0.106	0.252	0.256	84.1 ²	78.9 ²
ETPRF 20-12-58	0.200	0.120	0.581	0.099	0.392	0.129	0.402	0.077	102.6 ³	93.2 ³
ETPRF 20-16-27	0.200	0.158	0.270	0.372	0.377	0.163	0.180	0.279	81.0 ¹	75.8 ¹
ETPRF 20-20-25	0.200	0.200	0.253	0.347	0.372	0.204	0.166	0.258	84.2 ²	78.1 ²
ETPRF 20-24-43	0.200	0.238	0.426	0.136	0.374	0.244	0.281	0.101	101.4 ³	91.1 ³
ETPRF 20-32-4	0.200	0.322	0.045	0.434	0.354	0.312	0.028	0.306	78.3 ¹	70.5 ¹
ETPRF 20-36-28	0.200	0.360	0.278	0.162	0.357	0.352	0.175	0.116	100.2 ³	89.1 ³
ETPRF 20-40-4	0.200	0.400	0.037	0.363	0.347	0.380	0.023	0.251	85.4 ²	77.9 ²
ETPRF 40-6-28	0.400	0.061	0.284	0.256	0.629	0.053	0.158	0.160	97.8 ¹	87.8 ¹
ETPRF 40-9-44	0.400	0.090	0.436	0.074	0.632	0.078	0.243	0.047	107.1 ³	93.6 ³
ETPRF 40-10-26	0.400	0.100	0.263	0.237	0.623	0.085	0.145	0.147	98.2 ²	88.1 ²
ETPRF 40-12-20	0.400	0.119	0.203	0.279	0.617	0.100	0.111	0.172	96.8 ¹	86.6 ¹
ETPRF 40-18-32	0.400	0.179	0.319	0.102	0.614	0.150	0.173	0.062	106.0 ³	92.1 ³
ETPRF 40-20-17	0.400	0.200	0.168	0.232	0.605	0.166	0.090	0.140	99.2 ²	88.0 ²
ETPRF 40-24-3	0.400	0.241	0.034	0.325	0.594	0.196	0.018	0.192	94.4 ¹	84.3 ¹
ETPRF 40-27-21	0.400	0.270	0.208	0.122	0.597	0.221	0.110	0.072	104.6 ³	90.9 ³
ETPRF 40-40-2	0.400	0.400	0.019	0.181	0.573	0.314	0.009	0.104	103.6 ²	89.3 ²
ETPRF 60-4-19	0.600	0.041	0.189	0.170	0.792	0.030	0.088	0.090	105.2 ¹	88.5 ¹
ETPRF 60-6-29	0.600	0.060	0.290	0.050	0.794	0.043	0.136	0.026	107.7 ³	92.6 ³
ETPRF 60-8-14	0.600	0.079	0.135	0.186	0.784	0.057	0.062	0.097	104.4 ¹	89.7 ¹
ETPRF 60-10-16	0.600	0.100	0.158	0.142	0.782	0.071	0.073	0.074	105.1 ²	91.0 ²
ETPRF 60-12-21	0.600	0.119	0.213	0.068	0.782	0.085	0.098	0.035	107.1 ³	92.0 ³
ETPRF 60-16-2	0.600	0.161	0.022	0.217	0.767	0.113	0.010	0.110	103.4 ¹	88.4 ¹
ETPRF 60-18-14	0.600	0.180	0.139	0.081	0.769	0.126	0.063	0.041	106.3 ³	91.2 ³
ETPRF 60-20-8	0.600	0.200	0.084	0.116	0.764	0.139	0.038	0.059	107.0 ²	91.2 ²
ETPRF 60-40-0	0.600	0.400	0.000	0.000	0.733	0.267	0.000	0.000	110.7 ²	93.3 ²
ETPRF 80-3-15	0.800	0.030	0.145	0.025	0.912	0.019	0.059	0.011	107.8 ³	91.7 ³
ETPRF 80-6-11	0.800	0.060	0.106	0.034	0.905	0.037	0.043	0.015	107.5 ³	91.4 ³
ETPRF 80-9-7	0.800	0.090	0.069	0.041	0.899	0.055	0.028	0.018	107.1 ³	91.1 ³

¹ ASTM D2699, D2700 measurements [3, 4] in [31]² Blending rule in [31]³ ASTM D2699, D2700 measurements [3, 4] in [34]

Table S7: Fuel matrix of MCSB from [32]

Blend	Volume fraction					Mole fraction					RON ¹	MON ¹
	<i>iso</i> -Octane	Toluene	<i>n</i> -heptane	1-Hexene	124-TMB ²	CPT ³	<i>iso</i> -Octane	Toluene	<i>n</i> -Heptane	1-Hexene	124-TMB	CPT
MCSB 1	0.910	0.090	0.000	0.000	0.000	0.000	0.900	0.100	0.000	0.000	0.000	0.000
MCSB 2	0.725	0.125	0.150	0.000	0.000	0.000	0.660	0.128	0.212	0.000	0.000	0.000
MCSB 3	0.525	0.175	0.300	0.000	0.000	0.000	0.442	0.166	0.392	0.000	0.000	0.000
MCSB 4	0.847	0.051	0.000	0.102	0.000	0.000	0.815	0.055	0.000	0.130	0.000	0.000
MCSB 5	0.770	0.030	0.000	0.200	0.000	0.000	0.721	0.032	0.000	0.247	0.000	0.000
MCSB 6	0.650	0.100	0.150	0.100	0.000	0.000	0.576	0.100	0.207	0.117	0.000	0.000
MCSB 7	0.580	0.070	0.150	0.200	0.000	0.000	0.502	0.068	0.202	0.229	0.000	0.000
MCSB 8	0.465	0.139	0.319	0.077	0.000	0.000	0.382	0.128	0.407	0.083	0.000	0.000
MCSB 9	0.390	0.110	0.390	0.200	0.000	0.000	0.313	0.100	0.375	0.212	0.000	0.000
MCSB 10	0.760	0.090	0.000	0.000	0.150	0.000	0.729	0.097	0.000	0.000	0.173	0.000
MCSB 11	0.610	0.090	0.000	0.000	0.300	0.000	0.568	0.095	0.000	0.000	0.337	0.000
MCSB 12	0.750	0.100	0.080	0.000	0.070	0.000	0.700	0.105	0.116	0.000	0.079	0.000
MCSB 13	0.575	0.125	0.150	0.000	0.150	0.000	0.509	0.125	0.206	0.000	0.160	0.000
MCSB 14	0.810	0.090	0.000	0.000	0.000	0.100	0.744	0.093	0.000	0.000	0.000	0.163
MCSB 15	0.710	0.090	0.000	0.000	0.000	0.200	0.609	0.087	0.000	0.000	0.000	0.304
MCSB 16	0.620	0.130	0.150	0.000	0.000	0.100	0.527	0.125	0.198	0.000	0.000	0.150
MCSB 17	0.430	0.170	0.300	0.000	0.000	0.100	0.340	0.152	0.368	0.000	0.000	0.140
MCSB 18	0.510	0.140	0.150	0.000	0.000	0.200	0.406	0.126	0.186	0.000	0.000	0.282
MCSB 19	0.320	0.180	0.300	0.000	0.000	0.200	0.238	0.151	0.347	0.000	0.000	0.264
MCSB 20	0.700	0.300	0.000	0.000	0.000	0.000	0.674	0.326	0.000	0.000	0.000	0.000
MCSB 21	0.520	0.330	0.150	0.000	0.000	0.000	0.462	0.331	0.207	0.000	0.000	0.000
MCSB 22	0.300	0.400	0.300	0.000	0.000	0.000	0.246	0.371	0.383	0.000	0.000	0.000
MCSB 23	0.650	0.250	0.000	0.100	0.000	0.000	0.611	0.265	0.000	0.124	0.000	0.000
MCSB 24	0.570	0.230	0.000	0.200	0.000	0.000	0.521	0.237	0.000	0.242	0.000	0.000
MCSB 25	0.440	0.310	0.150	0.100	0.000	0.000	0.381	0.303	0.202	0.114	0.000	0.000
MCSB 26	0.360	0.290	0.150	0.200	0.000	0.000	0.304	0.276	0.197	0.223	0.000	0.000
MCSB 27	0.570	0.280	0.000	0.000	0.150	0.000	0.534	0.296	0.000	0.169	0.000	0.000
MCSB 28	0.410	0.290	0.000	0.000	0.300	0.000	0.373	0.298	0.000	0.329	0.000	0.000
MCSB 29	0.540	0.310	0.080	0.000	0.070	0.000	0.492	0.318	0.113	0.000	0.077	0.000
MCSB 30	0.360	0.340	0.177	0.000	0.124	0.000	0.309	0.329	0.235	0.000	0.128	0.000
MCSB 31	0.070	0.430	0.300	0.000	0.000	0.200	0.051	0.353	0.339	0.000	0.000	0.258
MCSB 32	0.360	0.340	0.150	0.000	0.150	0.000	0.311	0.331	0.201	0.000	0.156	0.000

¹ ASTM D2699, D2700 measurements [3, 4] performed at Saudi Aramco [32]

² 1,2,4-trimethylbenzene

³ Cyclopentane

Figure S1: RON space

Figure S2: MON space

Figure S3: Error in predictions of (a) RON and (b) MON with IDT calculated using the KAUST-LLNL-NUIG gasoline surrogate model [42] at 20 bar with reproducibility and repeatability limits

Figure S4: Exponent n and coefficients a , b in Eq. (2) to predict RON (left) and MON (right)

Figure S5: Error in predictions of RON with IDT calculated using the KAUST-LLNL-NUIG gasoline surrogate model [42] with reproducibility and repeatability limits

Figure S6: Error in predictions of MON with IDT calculated using the KAUST-LLNL-NUIG gasoline surrogate model [42] with reproducibility and repeatability limits

(a)

(b)

Figure S7: Predicted and nominal (a) RON and (b) MON of PRF, TRF and TPRF with IDT calculated using the KAUST-LLNL-NUIG gasoline surrogate model [42] at different pressures

(a)

(b)

Figure S8: Predicted and nominal (a) RON and (b) MON of ERF, EPRF and ETPRF with IDT calculated using the KAUST-LLNL- NUIG gasoline surrogate model [42] at different pressures

(a)

(b)

Figure S9: Predicted and nominal (a) RON and (b) MON of MCSB with IDT calculated using the KAUST-LLNL-NUIG gasoline surrogate model [42] at different pressures

Figure S10: Error in predictions of (a) RON and (b) MON with experimental IDT in Table 2 with reproducibility and repeatability limits

Figure S11: Comparison of R^2 of RON (top) and MON (bottom) predictions of various mixtures at different pressures

Figure S12: Comparison of RMSE of RON (top) and MON (bottom) predictions of various mixtures at different pressures

VALIDATION WITH TRF, TPRF AND PRF WITH OTHER KINETIC MODELS

The coefficients shown in Table 1 that were obtained from PRF, TRF and TPRF simulations were adopted for PRF, TRF and TPRF to predict RON and MON using Eq. (2); IDT is the simulated IDT of the chosen PRF, TRF and TPRF mixture. As previously mentioned, the coefficients were determined using IDT simulations of PRF using the KAUST-LLNL-NUIG gasoline surrogate model [42]. To test the rigor of the present methodology, we attempted to predict RON and MON of various TRF, TPRF, and PRF mixtures by simulation with their IDTs calculated using other chemical kinetic models. To this end, three models were selected and utilized in the present study, specifically: (i) the LLNL gasoline surrogate model [61], (ii) the RWTH optimized gasoline surrogate model [62], (iii) and the POLIMI PRF surrogate model [63]. As shown in the following discussion, RON and MON predicted using simulated IDT with different chemical kinetic models show close agreement with nominal values, with some deviations in lower octane number range.

Figures S13 and S14 shows comparison between predicted RON and MON respectively with nominal values where IDTs were calculated using the detailed LLNL gasoline surrogate model [61]. In this case also, predictions of RON and MON were remarkably close to the nominal values. Comparisons of predicted and nominal RON

and MON of PRFs, TRFs and TPRFs where IDTs were calculated using the RWTH optimized gasoline surrogate model [62] are shown in Figs. S15 and S16. In this case also, predictions of RON are remarkably close to the nominal values. Predictions of MON are reasonable at higher octane numbers. Even though the RWTH optimized gasoline surrogate model [62] not been validated at pressures higher than 40 bar, results are shown. For MON predictions, results at pressures higher than 40 bar indicate considerable differences with nominal values, which could be attributed to the model's ability to to reproduce IDT in the NTC regime at higher pressures. It is also interesting to note that predictions of TPRF are encompassed by predictions of TRF and PRF.

Figure S13: Predicted and nominal RON of PRF with IDT calculated using the LLNL gasoline surrogate model [61] at different pressures

Figure S14: Predicted and nominal MON of PRF with IDT calculated using the LLNL gasoline surrogate model [61] at different pressures

Figure S15: Predicted and nominal RON of PRF, TRF and TPRF with IDT calculated using the RWTH optimized gasoline surrogate model [62] at different pressures

Figure S16: Predicted and nominal MON of PRF, TRF and TPRF with IDT calculated using the RWTH optimized gasoline surrogate model [62] at different pressures

Predicted RON and MON of PRFs with IDT calculated using the POLIMI PRF model [63] is shown in Figs. S17 and S18, respectively. Only predictions of PRF are shown as the model has not been validated for TRF and TPRF mixtures. As can be observed in the figures, predictions of RON and MON are good even when IDT are simulated with a model other than that used to determine the coefficients in Eq. (2).

Figure S17: Predicted and nominal RON of PRF, TRF and TPRF with IDT calculated using the POLIMI PRF model [63] at different pressures

Figure S18: Predicted and nominal MON of PRF, TRF and TPRF with IDT calculated using the POLIMI PRF model [63] at different pressures

Figure S19: (a) RON and (b) MON space at $P_0 = 50$ bar

Figure S20: Uncertainty in estimation of (a) RON and (b) MON (bottom) at 20 and 40 bar with uncertainty in fit parameters given in Table 5. Inset represents higher ON range.

Figure S21: Uncertainty in estimation of RON (left) and MON (right) at different pressures with uncertainty in fit parameters given in Table 5. Inset represents higher ON range.

Figure S22: Uncertainty in estimation of RON (left) and MON (right) for $\pm 20\%$ uncertainty in IDT at different pressures with uncertainty in fit parameters given in Table 5. Inset represents higher ON range.