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Estimating fuel octane numbers from homogeneous gas-phase ignition delay times

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ABSTRACT

Fuel octane numbers are directly related to the autoignition properties of fuel/air mixtures in spark ignition (SI) engines. This work presents a methodology to estimate the research and the motor octane numbers (RON and MON) from homogeneous gas-phase 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, 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. Conditions in homogeneous reactors such as shock tubes and rapid compression machines that are relevant to modern SI engines were also identified. Uncertainty analysis of the proposed correlations with linear error propagation theory is also presented.

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 antiknock 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

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defined as

$$OI = (1-k)RON + kMON \tag{1a}$$

$$OI = RON - kS \tag{1b}$$

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 turbocharging and downsizing, 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 (ON) 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 [11–15], 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 [22–26] 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 [30,31,33,34].

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 $= \frac{RON+MON}{2}$) [35–38], density, and distillation characteristics [39–42]. 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 ONs.

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 the 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 particluar 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 factors 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 the 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