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A methodology to relate octane numbers of binary and ternary n-heptane, iso-octane and toluene mixtures with simulated ignition delay times

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HIGHLIGHTS

- Potential correlations between RON and MON and IDT for TPRF blends are investigated.
- Constant and variable volume ignition delay times are tested.
- The RON-like 850 K and 50 atm proposed conditions best correlated with the RON.
- The CR dependent volume profiles lead to better correlation with RON and MON.

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ABSTRACT

Predicting octane numbers (ON) of gasoline surrogate mixtures is of significant importance to the optimization and development of internal combustion (IC) engines. Most ON predictive tools utilize blending rules wherein measured octane numbers are fitted using linear or non-linear mixture fractions on a volumetric or molar basis. In this work, the octane numbers of various binary and ternary n-heptane/iso-octane/toluene blends, referred to as toluene primary reference fuel (TPRF) mixtures, are correlated with a fundamental chemical kinetic parameter, specifically, homogeneous gas-phase fuel/air ignition delay time. Ignition delay times for stoichiometric fuel/air mixtures are calculated at various constant volume conditions (835 K and 20 atm, 825 K and 25 atm, 850 K and 50 atm (research octane number RON-like) and 980 K and 45 atm (motor octane number MON-like)), and for variable volume profiles calculated from cooperative fuel research (CFR) engine pressure and temperature simulations. Compression ratio (or ON) dependent variable volume profile ignition delay times are investigated as well. The constant volume RON-like ignition delay times correlation with RON was the best amongst the other studied conditions. The variable volume ignition delay times condition correlates better with MON than the ignition delay times at the other tested conditions. The best correlation is achieved when using compression ratio dependent variable volume profiles to calculate the ignition delay times. Most of the predicted research octane numbers (RON) have uncertainties that are lower than the repeatability and reproducibility limits of the measurements. Motor octane number (MON) correlation generally has larger uncertainties than that of RON.

1. Introduction

As the global energy demand for transportation increases, so does the demand for more efficient automobile vehicles. One of the main concerns and limiting factors in the automotive industry is the engine knock phenomenon [1–3]. Engine knock, according to Morgan et al. [4], can be defined as a "limiting factor of a spark ignition (SI) engine's thermodynamic efficiency caused by the auto-ignition of the fuel/air mixture ahead of the turbulent flame front".

Practical fuels such as gasoline, diesel and jet fuels are complex mixtures of hundreds of different components. The autoignition

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chemistry of practical fuels is thus very complicated and difficult to predict accurately. Ignition delay time measurement devices, such as shock tubes (ST) and rapid compression machines (RCM), cannot be used to fully understand the knock phenomenon because these idealized reactors operate at near-constant volume reaction conditions. On the other hand, pressure and temperature evolve and cover wide range of conditions in practical devices such as engines. Therefore, fuel anti-knock quality has to be described by empirical measurements, known as Research and Motor Octane Numbers, RON and MON. These tests are run in a single-cylinder CFR (Cooperative Fuels Research) engine in accordance with the procedures set in ASTM D2699 for RON and ASTM D2770 for MON [5]. The RON test is run at an engine speed of 600 rpm and an intake temperature of 52 °C while the MON test is run at 900 rpm and a higher intake temperature of 149 °C.

Since commercial gasoline fuels consist of a range of compounds that are not universally consistent due to the differences in the crude oil origin and refinery processes [6], understanding the fuel behaviour becomes a multifaceted issue. To simplify this problem, it has been proposed that fuel behaviour can be modelled through simple mixtures (surrogates) that mimic the real fuel properties under certain conditions. Iso-octane is the simplest surrogate for gasoline and it is usually used to describe flame propagation [7]. However, the autoignition properties of real gasoline cannot be adequately described by iso-octane because of its high octane numbers (RON = MON = 100). Therefore, Primary Reference Fuels (PRFs), which are mixtures of n-heptane and iso-octane, are used to match the gasoline octane numbers. By definition, PRFs have zero sensitivity, where sensitivity is defined to be the difference of RON and MON (sensitivity = RON–MON). Hence, two different PRFs are needed to match real gasoline octane numbers under RON and MON conditions [8–10]. Real gasoline fuels have sensitivities up to 11 because they contain considerable amounts of branched paraffins, olefins and aromatics. Thus, a sensitive component must be added to PRF blends to match octane numbers and sensitivities of the real gasoline. Aromatics, such as toluene, are generally added to PRF blends to account for the missing sensitivity. Shock tube [11] and engine experiments [12] have demonstrated that blends of n-heptane/isoc-octane/toluene, known as toluene primary reference fuel (TPRF) blends, can adequately represent autoignition behaviour of gasoline [4,11,12]. Some researchers have proposed gasoline surrogates that contain more than three compounds. Mehl et al. [13] proposed a four component surrogate comprising n-heptane, iso-octane, toluene and 1-hexene (olefin) to represent the ignition behaviour of RD-387 gasoline. Perez and Boehman [14] investigated 5 component surrogates where they added methylcyclo-hexane (naphthenes) on top of the four components proposed by Mehl et al. [13]. Naik et al. [15] replaced 1-hexene with 1-pentene to formulate their 5 components surrogates similar to [14]. Fikri et al. [16] studied the effect of adding diisobutylene to TPRFs and Yahyaoui et al. [17] investigated mixtures containing iso-octane, toluene, 1-hexene and ethyl-tert-butyl-ether (ETBE). Recently, Sarathy et al. [18] and Ahmed et al. [19] proposed 5 and 6 component surrogates to reproduce the ignition delay characteristics of alkane-rich gasoline fuels.

Significant amount of work has been reported on TPRF surrogates and validated chemical kinetic models exist in literature [13,16,20], so this work focuses only on TPRFs. The methodology used to TPRF surrogate composition for a real gasoline is crucial in order to accurately determine the mixture's RON and MON. The most common method of blending the surrogate components (n-heptane, iso-octane, toluene) is through blending rules that are developed based on data fittings from various experimental data sets. Lately, a study conducted by Knop et al. [21] on octane number prediction methods of TPRF fuel mixtures found that the linear-by-mole blending rule produce the best results in terms of accuracy. The results from their proposed blending rule were compared with six different existing methods and previously published experimental data. Recently, Kalghatgi et al. [22] proposed a new non-linear-by-mole blending rule that was based on a wide range of CFR experimental data for TPRF mixtures. Although these methodologies prove to give reasonably accurate results in predicting the ON of TPRF, the addition of any other components, such as ethanol, to the mixture causes the blending rule to fail [14,23].

Several studies have focused on trying to link the ON from CFR engine to basic chemical kinetic parameters. Leppard [9] related the sensitivity of the fuel to the negative temperature coefficient (NTC) behaviour of various fuels. Curran et al. [24] and Mehl et al. [25] proposed that the ON might actually correlate with the critical compression ratio (CCR). Hori et al. [26,27] investigated possible relation between ON and ignition properties within micro-flow reactors (MFR). Furthermore, Mehl et al. [13] and Sarathy et al. [28] examined the possibility that ON might correlate with homogeneous gas-phase ignition delay times. Mehl et al. [13] tried to correlate the anti-knock index (AKI = (RON + MON)/2) with ignition delay times of stoichiometric fuel/air mixtures at 825 K and 25 atm, whereas Sarathy et al. [28] chose different conditions (835 K and 20 atm) to relate RON to homogeneous ignition delay times. Both authors utilized constant volume simulations for their correlations, while Sarathy et al. [28] also included experimental shock tube ignition delay data acquired for pure components (normal and branched alkanes) for the correlation.

The purpose of this study is to provide a methodology to associate a fuel's research octane number (RON) and motor octane number (MON) with the homogeneous gas-phase ignition delay times through the use of chemical kinetic simulations. Ignition delay times are calculated at various conditions to investigate possible correlation with ON. Constant volume ignition delay times were tested by using the previously proposed temperature and equivalence ratio conditions of Mehl et al. [13], Sarathy et al. [28] and newly proposed RON-like and MON-like conditions. Variable pressure and temperature profiles from CFR engine experiments were also tested. Finally, compression ratio and octane number dependent pressure and temperature profiles were investigated, and a promising correlation between ON and ignition delay times was obtained.

2. Prediction methodology and numerical approach

To obtain a correlation between ignition delay times and ON for TPRF fuels, CFR measurements in the literature were collected and used for the current analysis. Recently, our group published a new set of CFR experimental data for TPRF mixtures with the toluene concentration varying from 10% to 90% by volume [22]. For each toluene percentage, iso-octane (vol.%)/n-heptane (vol.%) was varied from 0 to 100. This experimental data set was utilized to develop a new non-linear by mole blending rule, which was validated against other data from literature [22]. In the current work, new CFR measurements were performed so that the prediction can cover a wider range of octane numbers. The newly collected data are primarily for n-heptane/toluene mixtures with varying toluene concentration from 10% to 80% by volume. Also, MON measurements for some TPRF mixtures were not provided in