

The Underlying Physics and Chemistry behind Fuel Sensitivity

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Vikram Mittal, John B. Heywood and William H. Green
Sloan Automotive Laboratory, Massachusetts Institute of Technology

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ABSTRACT

Recent studies have shown that for a given RON, fuels with a higher sensitivity (RON-MON) tend to have better antiknock performance at most knock-limited conditions in modern engines. The underlying chemistry behind fuel sensitivity was therefore investigated to understand why this trend occurs. Chemical kinetic models were used to study fuels of varying sensitivities; in particular their autoignition delay times and chemical intermediates were compared.

As is well known, non-sensitive fuels tend to be paraffins, while the higher sensitivity fuels tend to be olefins, aromatics, diolefins, napthenes, and alcohols. A more exact relationship between sensitivity and the fuel's chemical structure was not found to be apparent. High sensitivity fuels can have vastly different chemical structures.

The results showed that the autoignition delay time (τ) behaved differently at different temperatures. At temperatures below 775 K and above 900 K, τ has a strong temperature dependence. However, between 775 K and 900 K, τ has a decreased temperature dependence. The change in temperature dependence in this region was found to correlate with fuel sensitivity. The autoignition of fuels with a higher sensitivity have a higher temperature dependence in that region. A stronger temperature dependence on τ in this region results in slower low temperature chemistry and faster high temperature chemistry.

As a consequence, fuels behave differently depending on the temperature regime of the end-gas. If two fuels have the same RON, the autoignition integral for the two fuels approaches 1 at the same time in the RON test. Lower end-gas temperatures would allow sensitive fuels, which have slower

low temperature chemistry, to have better antiknock performance. However, higher end-gas temperatures, such as those in the MON test, would allow non-sensitive fuels to have better antiknock performance.

The fuels with larger sensitivities studied here were predicted by kinetic models to produce large amounts of aldehydes, which are relatively stable at low temperatures, but react rapidly at high temperatures. These aldehydes appear to be an important cause of the octane sensitivity.

INTRODUCTION

The term knock refers to the engine noise caused by the rapid autoignition of the end-gas, the unburned fuel-air mixture ahead of the flame, in a spark ignition engine [1]. The noise is created by the rapid pressure rise and oscillations caused by autoignition. Typically, knock is an annoying metallic clanking noise, and heavier knock can be an indication that engine damage is occurring. In order to avoid knock, it is necessary to use fuels that are resistant to the autoignition process.

A fuel's propensity to autoignite and cause knock is quantified in terms of an octane index (OI). The concept behind the OI is that a fuel's complex autoignition chemistry can be compared to a binary fuel blend which would have a predictable autoignition behavior. The binary blend used in these comparisons is a primary reference fuel (PRF), a blend of iso-octane and n-heptane*. As the percentage of iso-octane increases in the blend, the fuel mixture is less prone to autoignition. The OI of a fuel is defined as the volumetric percentage of iso-octane in the PRF that knocks at the same intensity at the same conditions. [1]

*The naming convention for a PRF is that PRFX is a blend of X percent by volume of iso-octane and (100-X) percent of n-heptane. PRF96 therefore is 96 percent iso-octane and 4 percent n-heptane by volume.

If at a given engine operating condition, a fuel's knocking behavior is similar to a blend of 96 percent iso-octane, 4 percent n-heptane (PRF96), the fuel would have an OI of 96. However, at another engine operating condition, the fuel could behave similar to PRF87 and hence have an OI of 87.

Since the OI depends on the engine operating conditions, it is measured at two standardized test conditions for fuel rating purposes. These two conditions are the Research and Motor Octane Number (RON and MON) tests, which are described in detail in [2] and [3] respectively.

The tests are done in a Cooperative Fuel Research (CFR) engine at the conditions shown in Table 1. The inlet conditions and engine speed are fixed, and the compression ratio is increased until the engine knocks at a given intensity. The procedure is then repeated for different PRFs until a PRF is found that knocks at the same intensity at the same compression ratio. The RON and MON of the fuel are the Octane Indices measured in these specific tests [2,3].

The compression ratio in the octane tests vary with the fuel's octane number; therefore, the peak pressure and temperature in these tests vary with the fuel. Therefore, the peak temperature in the RON96 test is significantly higher than the peak temperatures in the RON87 test.

The two main differences between the RON and MON tests are the intake air temperature and the engine speed. Modern engines have intake air temperatures that are well below the RON and MON tests. In particular, the intake air temperature of the MON test is over 100°C above that of modern engines. Additionally, though cars can idle at 600 rpm, they seldom operate at full load at engine speeds below 1200 rpm.

The difference between the RON and MON is termed the sensitivity, S:

$$S = \text{RON} - \text{MON} \quad (1)$$

By the definition of the octane number, the sensitivity of a PRF is 0. However, most commercial fuels have a sensitivity of about 8 [1].

Since the RON and MON are the OI of a fuel at two set conditions, the OI can be interpolated from these values using a weighing factor, K:

$$\text{OI} = (1-K) \text{RON} + K \text{MON} = \text{RON} - K \times S \quad (2)$$

K is assumed to be independent of the fuel, depending only on the engine's operating condition [4]. It should be noted that K = 0 corresponds to the RON test and K = 1 corresponds to the MON test. Since the OI posted on retail

gasoline dispensers in the United States is (R+M)/2, the value of K = 0.5 is used to define a fuel's "on the road" octane number in the US.

An experimental study presented in previous works [4,5] found most modern knock-limited operating conditions have OI's that require $K < 0$ in Eq. 2. Therefore, in modern engines, for a given RON, fuels with a higher sensitivity (i.e. lower MON) have better antiknock performance.

Table 1. The engine conditions for the RON and MON tests

Parameter	RON	MON
Intake Air Temperature	52°C	149°C
Intake Air Pressure	atmospheric	atmospheric
Coolant Temperature	100°C	100°C
Engine Speed	600 rpm	900 rpm
Spark Timing	13° BTC	14-26° BTC
Compression Ratio	4-18	4-18

CHEMICAL MODELS

Chemical kinetic models can be used to analyze the chemistry of autoignition at different thermodynamic conditions. These models are useful in characterizing autoignition in terms of an autoignition delay time (τ). The autoignition delay time is the induction time required for a fuel and air mixture to react and autoignite. Usually, τ is approximated to have the form [1]:

$$\tau = c_1 p^{-c_2} \exp(c_3/T) \quad (3)$$

such that the value of τ decreases as pressure and temperature increase. Since τ is a function of temperature and pressure, both of which are changing inside of an engine, the Livengood-Wu autoignition integral is often used for estimating in ignition delays. By this model, autoignition occurs when:

$$\int_{\tau} \frac{1}{\tau} dt = \int \frac{1}{N\tau} d\theta = 1 \quad (4)$$

where N is the engine speed, t is time, and θ is the CAD.

The constants in Eq. 3 were determined by Douaud/Eyzat [6] to be: $c_1 = 17.68 \times (\text{ON}/100)^{3.402}$, $c_2 = -1.7$, $c_3 = 3800$. These constants were based on measurements with PRFs, and hence the RON and the MON are the same; therefore, the ON term in c_1 refers to either the RON or the MON. In practice, it was found that Eqs 3 and 4, when using the average of the RON and MON (i.e. $K=0.5$ in Eq. 2) in c_1 , are useful for predicting autoignition [7]. However, it is known that τ does not

precisely follow Eqs 3 and 4, particularly from 775 to 900 K, so a more detailed analysis is required.

If the composition of the fuel is known, and a chemical kinetic model for that fuel is available, the value of τ for a fuel and air mixture at a given temperature and pressure can be determined by the constant pressure batch reactor model shown in Fig. 1. In the reactor, a perfectly mixed blend of fuel and air is held at a constant pressure, and the autoignition delay time is computed. Though the initial temperature is specified, the temperature rises due to chemical heat release.

The constant pressure batch reactor in Fig. 1 can be modified to better represent the conditions of the end-gas in an engine. First, a pressure and adiabatic end-gas temperature trace from an engine simulation model are discretized into small finite time steps. A constant pressure batch reactor is then run for the first time step at the initial temperature and pressure. The products at the end of the time step are the reactants for the next time step. This process repeats until autoignition occurs, as shown in Fig. 2.

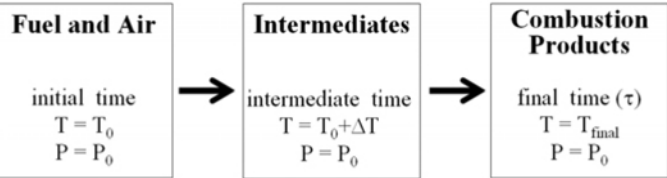


Figure 1. Constant pressure batch reactor. The temperature is free to increase with chemical heat release, but the pressure remains constant.

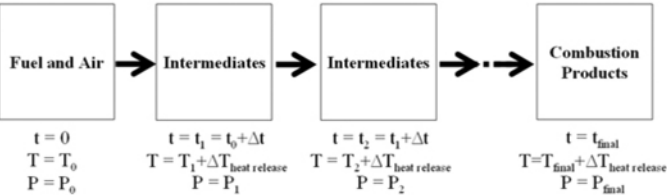


Figure 2. Model used to simulate changing charge pressures and temperatures inside an engine. At each time step, the pressure and temperature are increased.

Chemical kinetic models were run with the fuel blends listed in Table 2. These fuel blends are composed of iso-octane, n-heptane, toluene, and ethanol, and were chosen from those tested in [5] which had components with detailed chemical kinetic mechanisms available. Each fuel has a RON of 96 with a sensitivity ranging from 0 to 17.

Different sets of chemical kinetic mechanisms were used to look at the autoignition of these fuel blends. The first mechanism is the reduced chemical kinetic mechanism for iso-octane and n-heptane, developed by Tanaka et al. [8].

This mechanism has 67 reactions with 32 species. The reduced mechanism was used to look at larger trends and to validate the modeling code. The second mechanism is the detailed chemical kinetic mechanism developed by Andrae [9] to predict the autoignition of iso-octane, n-heptane, and toluene blends. This mechanism was merged with the mechanism developed by Marinov [10] for ethanol, to produce a mechanism with 4465 reactions and 1050 species. The final mechanism used was developed by Sakai [11] and contains the chemical kinetics of iso-octane, n-heptane, toluene, and ethanol oxidation. This mechanism contains 2877 reactions and 807 species.

Table 2. The fuel blends used in this study. The fuels are blends of iso-octane, n-heptane, toluene, and ethanol, each with a RON of 96 and a sensitivity ranging from 0 to 17.

Fuel	RON	MON	(R+M)/2	S
PRF96	96.0	96.0	96.0	0.0
11% n-heptane, 53% iso-octane, 36% toluene	96.2	91.3	93.8	4.9
16% n-heptane, 28% iso-octane, 56% toluene	96.1	88.4	92.3	7.7
22% n-heptane, 0% iso-octane, 78% toluene	96.1	84.5	90.3	11.6
63.5% ethanol, 36.5% n-heptane	96.0	79.0	87.5	17.0

The detailed chemical analysis presented in this study is based on the Sakai mechanism. However, the same analysis was also done with the Andrae/Marinov mechanism, which gave similar results.

The matrices describing the chemical reactions were set-up using OpenChemPro [12]. These matrices were then solved using Jacobian [13].

PROPERTIES OF INDIVIDUAL FUEL COMPONENTS

Many studies have been performed to relate the chemical structure of fuels to their autoignition chemistry. While there has been significant progress [14], few generalizations have been shown to hold up for all cases. In particular, it is often found that 2 molecules with identical chemical formulas and very similar structure have different OIs.

Figure 3 plots the RON against the MON for a number of different types of pure hydrocarbons. Non-sensitive fuels are on the black line, and sensitive fuels are below the black line, since their RON is greater than their MON. The plot shows that the non-sensitive fuels tend to be paraffins. This trend occurs because the RON and MON tests were designed such that blends of iso-octane and n-heptane would have an