

Exploring the Relationship Between Octane Sensitivity and Heat-of-Vaporization

C. Scott Sluder and James P. Szybist
Oak Ridge National Laboratory

Robert L. McCormick, Matthew A. Ratcliff, and Bradley T. Zigler
National Renewable Energy Laboratory

ABSTRACT

The latent heat-of-vaporization (HoV) of blends of biofuel and hydrocarbon components into gasolines has recently experienced expanded interest because of the potential for increased HoV to increase fuel knock resistance in direct-injection (DI) engines. Several studies have been conducted, with some studies identifying an additional anti-knock benefit from HoV and others failing to arrive at the same conclusion. Consideration of these studies holistically shows that they can be grouped according to the level of fuel octane sensitivity variation within their fuel matrices. When comparing fuels of different octane sensitivity significant additional anti-knock benefits associated with HoV are sometimes observed. Studies that fix the octane sensitivity find that HoV does not produce additional anti-knock benefit. New studies were performed at ORNL and NREL to further investigate the relationship between HoV and octane sensitivity. Three fuels were formulated for the ORNL study with matched RON and octane sensitivity, but with differing HoV. Experiments with these fuels in a 1.6-liter GTDI engine showed that the fuels exhibited very similar combustion phasing under knock-limited spark advance (KLSA) conditions. Fuels having a range of RON, octane sensitivity, and HoV were tested at NREL in a single-cylinder GDI engine under conditions where octane sensitivity has little effect on knock resistance. KLSA was found to be well correlated with RON. These results reinforce the concept that HoV anti-knock effects can be viewed as a contributor to octane sensitivity. From this viewpoint, HoV effects manifest themselves as increases in octane sensitivity.

CITATION: Sluder, C., Szybist, J., McCormick, R., Ratcliff, M. et al., "Exploring the Relationship Between Octane Sensitivity and Heat-of-Vaporization," *SAE Int. J. Fuels Lubr.* 9(1):2016, doi:10.4271/2016-01-0836.

INTRODUCTION

Increasing the efficiency of spark-ignited (SI) engines is a priority for reducing petroleum consumption and reducing greenhouse gas emissions from transportation. The technologies typically employed to improve efficiency include direct injection (DI), down-sizing, down-speeding, turbocharging, and increased compression ratio. With the exception of DI, these technologies cause increased end-gas temperatures and pressures such that a more highly knock resistant fuel is needed for operation at optimal spark timing over a larger portion of the engine's speed-load range. The tendency of a SI engine fuel to resist autoignition (resist knock) is measured as the octane number. Octane number at retail pumps in the United States is given as the anti-knock index (AKI), the average of research octane number (RON) and motor octane number (MON). [1, 2] The differences between the RON and MON tests are intake charge temperature, spark timing, and engine speed. RON is measured at relatively lower intake temperature and slower engine speed while the MON is measured at relatively higher intake temperature and faster engine speed. In both tests the compression ratio at a standard knock intensity for the test fuel is compared to results for a set of primary reference fuels (PRFs). The PRFs are blends of isooctane (assigned RON and MON of 100) and n-heptane (assigned a RON and MON of 0).

The difference between RON and MON is called octane sensitivity (also often referred to as sensitivity), $S = \text{RON} - \text{MON}$. For the PRFs, $S=0$ but for almost all real fuels $S>0$. Because the paraffinic PRFs exhibit negative temperature coefficient behavior (the ignition delay increases rather than decreases as temperature is increased within a specific temperature range), the paraffins can be thought of as being super-rated on the higher end-gas temperature MON test. [3] Negative temperature coefficient behavior is significantly less likely for fuels containing olefins, aromatics, and ethanol such as real-world gasoline. As a consequence, S can be thought of as the sensitivity of the fuel autoignition kinetics to the unburned gas temperature. [4] For example, increasing the intake air temperature advances autoignition timing for all fuels, but the effect is much less pronounced for fuels with low S than for fuels with high S. It has also been shown that fuels with higher S have slower autoignition kinetics at lower temperatures and faster autoignition kinetics at higher temperatures, than do fuels with lower S. [5] Modern engines operate under conditions such that increasing MON at constant RON may actually lower the fuel knock resistance. [4, 6] Kalghatgi suggests that for modern engines knock resistance can be described more meaningfully in terms of an octane index (OI), where $\text{OI} = \text{RON} - K \cdot S$, which is not a fuel property but a function of the temperature-pressure history

that the fuel-air mixture experiences in the engine. [5] For modern and future SI engines K is typically negative, consistent with the observation that fuels with the same RON but higher S provide greater knock resistance. [6]

Fuel Evaporation Impacts in DI Engines

Fuel knock resistance for DI engines is enhanced by cooling of the fuel-air charge as the fuel evaporates. Because gas compression in an engine is ideally isentropic, reducing the initial mixture temperature reduces the end-gas temperature and enhances knock resistance. Evaporative cooling has other effects that can impact engine efficiency such as increasing intake charge density, reducing heat transfer at part load, and reducing the need for enrichment at high load, retarded combustion phasing conditions. [7, 8, 9] Exploiting these effects is a major advantage of DI engines. However, at 25°C, the HoVs of gasoline boiling range hydrocarbons are around 350 kJ/kg while that of ethanol is 920 kJ/kg. [10, 11] Because ethanol reduces the required air-to-fuel ratio for stoichiometric operation, the heat of vaporization advantage is even greater when considered on a per kilogram of stoichiometric mixture basis where the value for hydrocarbon is 22 kJ/kg while that for ethanol is 92 kJ/kg. [10] Chupka and coworkers have recently reported measurements of HoV for a range of gasoline hydrocarbon blendstocks and ethanol blends up to E50. [12] They found that the hydrocarbon blendstocks tested all had approximately the same HoV for temperatures up to 150°C and had the same response to blending with ethanol. HoV increased linearly with ethanol content from about 350 kJ/kg for E0 to about 670 kJ/kg for E50 at 25°C.

Modern DI engines use fuel injection strategies that balance competing objectives. For example, reducing the formation of particulate matter (PM) is a key objective, as is knock avoidance, improving volumetric efficiency, and of course control of noise, vibration, and harshness (NVH). Many, if not most, DI engines use a strategy that injects fuel during the intake stroke under most operating conditions. A portion of the injected fuel promptly evaporates, prior to closure of the intake valves. The remainder of the fuel, owing to the distillation characteristics of the fuel in use, droplet size, in-cylinder motion, and so on, evaporates after the intake valve closes.

The portion of the injected fuel that evaporates while the intake valve remains open cools and therefore increases the charge density inside the cylinder. This process may lead to improvement of the volumetric efficiency, as it can have the effect of increasing the trapped air mass at intake valve closure, at least at wide-open-throttle (WOT) conditions. At fixed torque output conditions, however, this effect may be reduced depending upon the throttle, turbocharger wastegate, and variable valve actuation strategies being employed. In such cases, the HoV effect on volumetric efficiency may not be observable during part-throttle operation. Since the intake air is cooled inside the cylinder, this portion of fuel also aids in knock reduction.

Injected fuel that evaporates after the intake valve closes further cools and increases the density of the trapped air charge, but cannot impact volumetric efficiency. Charge densification at this point in the cycle may reduce the work done by the piston on the trapped charge during

the compression process. This effect thus acts primarily to reduce the temperature of the trapped charge, potentially leading to improved anti-knock performance.

Fuel charge evaporation is influenced both by fuel characteristics (such as the distillation curve) and by engine characteristics (heat transfer, intake manifold temperatures, fuel injection pressures, etc). For this discussion, fuel evaporation is discussed in terms of the fractions of the fuel charge that fully evaporate before the intake valve closes and the remaining fraction that evaporates after the intake valve closes. The significance of these fractions in terms of knock avoidance depends upon how much of the heat of vaporization the fuel draws from the fresh air charge compared to the amount it draws from the hot surfaces of the cylinder bore or piston crown. Both of these fractions of the fuel potentially contribute to a knock-avoidance benefit, though their efficacy in this regard is not necessarily the same.

Fuel Evaporation Impacts in CFR Engines

The previous section discussed the potential for fuel that evaporates during the intake stroke to increase the volumetric efficiency in DI engines. RON and MON tests are conducted in a standardized platform, the Cooperative Fuel Research, or CFR, engine. The CFR engine was developed in the 1920s and has been the mainstay for octane rating tests ever since. CFR engines introduce fuel to the intake air using a carburetor. The RON procedure measures the antiknock quality of a fuel while the intake air temperature is maintained at 52 °C. The MON procedure measures the anti-knock quality of a fuel while the intake *mixture* temperature is maintained at 149 °C. The elevated mixture temperature of the MON test eliminates HoV effects. The RON test may include HoV effects, since changes in intake charge temperature resulting from fuel evaporation are possible.

As discussed previously, the introduction of ethanol into fuel raises the possibility for differences in fuel HoV to impact engine operation either through differences in anti-knock behavior or through differences in volumetric efficiency. Increasing volumetric efficiency in the RON test is one issue that could cause the high HoV fuels to be marginally under-rated. That is, the measured RON may be marginally lower than it would be if no volumetric efficiency improvement had taken place. The RON test is conducted at wide-open-throttle conditions, and so decreasing the mixture temperature will cause volumetric efficiency to increase. The increasing volumetric efficiency results in combustion of a greater mass of air/fuel mixture, resulting in higher end-gas temperatures in the unburned gases in the cylinder. Knock propensity increases with end-gas temperature. Thus, increasing volumetric efficiency may lead to the need to reduce compression ratio in the RON test to avoid knock, resulting in a marginally lower RON rating if fuel evaporation increases volumetric efficiency. Historically, this possibility was not relevant, since the HoV values of non-oxygenated hydrocarbons are similar. The addition of oxygenates, such as ethanol, raises the possibility of previously unanticipated volumetric efficiency effects. However end-gas temperature is also a function of the heat-of-combustion (HoC) value of the fuel. The addition of oxygenates lowers the fuel HoC value compared to

those of non-oxygenated hydrocarbons. These effects produce competing impacts in the RON rating test that under most conditions should partially offset one another. Nevertheless, the possibility of differences in octane rating caused by HoV and HoC differences as compared with non-oxygenated fuels cannot be dismissed. In some cases, these differences may result in marginal under-rating of oxygenated fuel blends.

Combustion Phasing and Knock Avoidance

The location in crank-angle space in the cycle where 50% of the fuel mass has burned (on an energy basis) is often termed CA50. At low loads where combustion is not knock-limited, CA50 is frequently located at 5-8 crank angle degrees (CAD) after top dead-center (ATDC). [13] Spark timing that results in CA50 in this range is referred to as minimum advance for best torque (MBT) and is the optimum timing for efficiency. [14] As the engine encounters knock, combustion is delayed (or retarded) by delaying the commanded spark timing. This delay reduces the pressure and temperature ahead of the flame front. Since end-gas knock is a kinetically-driven process, this reduction in pressure and temperature reduces knock intensity. Retarding CA50 timing also reduces engine efficiency, and so utilization of a fuel that has greater knock resistance lowers the amount of timing retard needed, and thus improves engine efficiency.

OVERVIEW OF PREVIOUS STUDIES ON HOV EFFECTS ON ENGINE KNOCK LIMIT

There have been several previous studies that sought to identify and quantify the HoV impact, if any, on fuel anti-knock performance.

MIT Study

A study by Kasseris and Heywood published in 2012 sought to quantify charge cooling effects on knock limits in DI engines. [15, 16] In this study, differences in knock resistance were investigated in a GM 2.0 liter LNF Ecotec engine. The engine was modified by the addition of port fuel injection (PFI) to augment the DI fuel system that was standard equipment for the production LNF engine and the addition of an electric heater to the intake system to allow independent adjustments to the intake air temperature. Fuel injection events were at a fixed location during the intake stroke. The fuels in this study were generated through splash-blending ethanol with a Haltermann 97-RON test gasoline to generate blends that ranged from no ethanol (E0) to 85% ethanol (E85). Though the RON and octane sensitivity of the ethanol blends are not listed in either publication, both fuel properties should increase significantly with increased ethanol content.

Fuels were introduced to the engine through either the PFI or DI fuel systems. When a given fuel was introduced through the DI system, the onset of knock was noted to move to higher pressures and temperatures compared with fuel introduced through the PFI system at the same intake air temperature. This shift is consistent with an impact from HoV in the DI case. For each fuel, data were collected using the DI system with the intake air heated to an elevated temperature so that the onset of knock returned to the same pressure condition as noted with the PFI experiments. Thus, data were

generated that described the apparent air temperature that “canceled out” the HoV effect present when DI was used. These experiments were then repeated for fuels of varying ethanol content that should exhibit a relatively large spread in their HoV values, and produced a curve that described the effective charge cooling at knock onset as a function of the fuel ethanol content.

The effective charge cooling was observed to be just over 10 °C for E0. E20 produced a charge cooling effect of approximately 16 °C, and the effect became more pronounced at E50 (30 °C) and E85 (49 °C). They estimated that these values were approximately 70% of the cooling that would occur for ideal adiabatic evaporation of fuel into a stoichiometric mass of air. Thus, this study observed that there was an apparent anti-knock benefit from HoV in DI engines, but with fuels for which changes in octane sensitivity and HoV are covariant.

Ford / AVL Study - Single-Cylinder Engine

Three studies published by Ford and AVL have also sought to evaluate charge cooling effects. The first of these was conducted using a single-cylinder research engine equipped with a DI fuel system. [9] This paper focused on a study to separate and quantify the relative effects of chemical octane rating and HoV on anti-knock quality of fuels. The specific details of the engine used in this study had been previously published, as it originated in a related study that investigated periodic addition of E85 to the cylinder as an anti-knock enhancement. [17] The engine was typical of modern DI engines in that it featured a 4-valve per cylinder, pent-roof, high-tumble cylinder design. It was also equipped with variable cam timing for both intake and exhaust valves. Similar to the MIT study engine, this engine was equipped with both PFI and DI fuel systems, and was additionally outfitted with an “upstream” fueling system analogous to a throttle-body fueling system. Fuel injection events in this study were during the intake stroke. This study included a very large fuel matrix in which ethanol was splash-blended at various concentrations into hydrocarbon blendstocks that varied in octane number. [18] Most study data was collected using blends of ethanol into an 88 RON blendstock.

The study used upstream fuel injection (UFI) compared with PFI and DI experiments combined with mixture temperature control to separate the chemical octane number effects from HoV effects on fuel anti-knock properties. One very well-known outcome of this study was that the charge cooling effect produced by an ethanol blend was of approximately the same magnitude as the chemical octane number effect. This finding was derived from comparison of the UFI data for E0 (88 RON blendstock) compared to the UFI and DI results for an E50 fuel derived from that same blendstock. Notably, the DI results for the E0 fuel showed only small differences compared with the UFI results, indicating that for E0 very little charge cooling effect was present. Calculation of the difference between the UFI and DI results for in-cylinder temperature showed a 30 °C charge temperature difference at the beginning of the compression stroke when the E50 fuel was used. This difference is in agreement with the observed intake air temperature difference for E50 in the MIT study discussed previously. The octane sensitivity and HoV for the E50 fuel were significantly higher than for E0. Hence, this finding is consistent with the effect with fuels for which HoV and octane sensitivity were

covariant. The authors also noted improved performance (higher load achieved with less spark retard) under full load retarded timing conditions for a matched RON, but high S and high HoV E30 blend. They theorized that HoV amplified the effect of S at retarded phasing, i.e. lower end gas temperatures relative to MBT conditions. The study also found significant benefit from HoV cooling in avoiding enrichment at high-load, retarded timing conditions.

Ford / AVL Study - Multi-Cylinder Engine

Two subsequent studies by Ford and AVL were conducted in a production 3.5-liter Ecoboost gasoline turbocharged direct-injection (GTDI) engine. [8, 13] These studies included two sets of fuels: one set that allowed the RON and MON of the ethanol blends to increase as the ethanol content increased from 10 to 30%, and another set that included fuels that were blended to closely match RON and MON as the ethanol content increased from 10 to 30%. This fuel set additionally included a 98 RON E10 and a 108 RON E85 fuel blend.

Experiments with the splash-blended fuels (with RON, octane sensitivity, and HoV covariant with ethanol content) produced combustion phasing trends that were consistent with the RON levels for the three fuels. In this case, it is not possible to separate RON and HoV effects on anti-knock performance.

When the fuels with well-matched RON and MON were run in the engine, the knock-limited combustion phasing was found to agree closely from one fuel to another. Thus, in this case no additional HoV effect is observed. The paper concludes that the HoV effect, if any, was captured in the RON ratings for the fuels (ethanol content up to E30). These fuels had moderate octane sensitivity levels that only varied from 7.4 to 8.0. Thus, this study demonstrates that when ethanol blending is conducted such that the variation in octane sensitivity is small, no additional HoV effect is observed.

University of Melbourne / Princeton University Study

A study by Foong at the University of Melbourne examined the question of charge cooling in a more fundamental approach using a CFR octane rating engine. [19] Experiments were conducted under the standardized RON and MON test procedures as well as a Modified RON test. Ethanol blends with gasoline, iso-octane, and nheptane were used as fuels for the study. The RON and octane sensitivity of the blends increased as ethanol was added to the fuel.

Monitoring of the intake mixture temperatures for the various fuel blends under RON test conditions showed that the mixture temperature dropped as a result of fuel evaporation; the change in temperature observed was dependent upon the ethanol content of the fuel blend. For ethanol-free blends, the intake mixture temperature averaged 38 °C, a drop of 14 °C resulting from the

evaporation of fuel into the temperature-controlled intake air. The mixture temperature continued to decline as the ethanol content increased to approximately 40 vol%, at which point the mixture temperature stabilized at approximately a 30 °C. Adding ethanol beyond this point did not cause the mixture temperature to drop further, indicating that fuel droplets were no longer completely evaporating upstream of the intake valve. This observed temperature drop at 40 - 50% ethanol content agrees well with those noted in the previously discussed studies.

A modified RON test was conceived based on the RON test results. The modified RON test uses a varying intake air temperature that caused the mixture temperature (after fuel addition) to be equal to 38 °C. When these conditions are applied to the intake, the modified RON result is found to be only marginally lower than the standard RON result for fuels containing less than 30% ethanol. As the ethanol content increased further, the modified RON and standard RON results diverged, with the modified RON result being the lower of the two measurements. For E100, the difference in results from the standard RON and modified RON tests was about 5 octane numbers, while this difference was about 1 octane number for E30. These data are reproduced in Figure 1 for use in discussions in this paper.

OVERVIEW OF STUDIES AT ORNL AND NREL

Results generated from studies at Oak Ridge National Laboratory (ORNL) and the National Renewable Energy Laboratory (NREL) have been analyzed to provide additional data for exploration of the relationship between octane sensitivity and HoV.

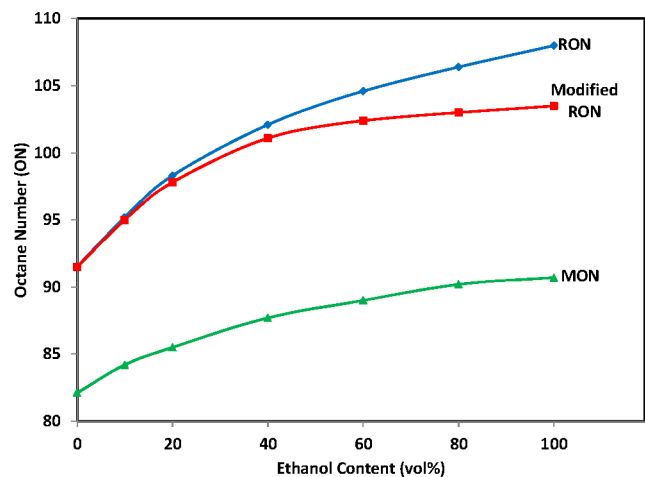


Figure 1. Results from a University of Melbourne study of RON, Modified RON, and MON for ethanol-gasoline blends. [19]

Oak Ridge National Laboratory Study

A study has been undertaken at ORNL to investigate potential efficiency advantages posed by fuels with increased octane number. As a part of this study experiments were conducted with fuels that have matched RON and octane sensitivity, but differing biofuel blending streams and HoV. The fuels were studied in a Ford Ecoboost