

Knock Resistance and Fine Particle Emissions for Several Biomass-Derived Oxygenates in a Direct-Injection Spark-Ignition Engine

Matthew A. Ratcliff, Jonathan Burton, Petr Sindler, Earl Christensen, Lisa Fouts,
Gina M. Chupka, and Robert L. McCormick
National Renewable Energy Laboratory

ABSTRACT

Several high octane number oxygenates that could be derived from biomass were blended with gasoline and examined for performance properties and their impact on knock resistance and fine particle emissions in a single cylinder direct-injection spark-ignition engine. The oxygenates included ethanol, isobutanol, anisole, 4-methylanisole, 2-phenylethanol, 2,5-dimethyl furan, and 2,4-xylene. These were blended into a summertime blendstock for oxygenate blending at levels ranging from 10 to 50 percent by volume. The base gasoline, its blends with p-xylene and p-cymene, and high-octane racing gasoline were tested as controls. Relevant gasoline properties including research octane number (RON), motor octane number, distillation curve, and vapor pressure were measured. Detailed hydrocarbon analysis was used to estimate heat of vaporization and particulate matter index (PMI). Experiments were conducted to measure knock-limited spark advance and particulate matter (PM) emissions. The results show a range of knock resistances that correlate well with RON. Molecules with relatively low boiling point and high vapor pressure had little effect on PM emissions. In contrast, the aromatic oxygenates caused significant increases in PM emissions (factors of 2 to 5) relative to the base gasoline. Thus, any effect of their oxygen atom on increasing local air-fuel ratio was outweighed by their low vapor pressure and high double-bond equivalent values. For most fuels and oxygenate blend components, PMI was a good predictor of PM emissions. However, the high boiling point, low vapor pressure oxygenates 2-phenylethanol and 2,4-xylene produced lower PM emissions than predicted by PMI. This was likely because they did not fully evaporate and combust, and instead were swept into the lube oil.

CITATION: Ratcliff, M., Burton, J., Sindler, P., Christensen, E. et al., "Knock Resistance and Fine Particle Emissions for Several Biomass-Derived Oxygenates in a Direct-Injection Spark-Ignition Engine," *SAE Int. J. Fuels Lubr.* 9(1):2016, doi:10.4271/2016-01-0705.

INTRODUCTION

A number of factors are currently converging to compel significant changes in automobile spark-ignition (SI) fuel and engine technology. Concerns regarding global climate change caused by greenhouse gas emissions [1] are leading to legislation in many countries mandating the use of low-net carbon emission fuels, primarily biofuels [2]. In the United States, for example, renewable fuel usage is mandated to increase under the Renewable Fuel Standard [3]. The same climate change concerns are driving the introduction of more stringent standards for fuel economy as well as greenhouse gas emissions at the tailpipe [4]; this in turn is driving research to increase the efficiency of SI engines. High-efficiency SI engines will apply a number of different technologies, including direct injection (DI), which takes advantage of evaporative cooling of the intake charge to reduce engine knock, allowing an increase in boost pressure and/or compression ratio [5]. Further increases in boost pressure and compression ratio (and consequently efficiency) require use of more highly knock-resistant fuel to maintain optimal or near optimal combustion phasing.

The ability of an SI engine fuel to resist autoignition and avoid knock is measured as octane number, a critical performance parameter for SI engines. In the United States, the octane number used for retail

gasoline is the anti-knock index, which is the average of the research octane number (RON) (ASTM D2699-13b) and motor octane number (MON) (ASTM D2700-13b). The primary differences between the RON and MON measurements are intake charge temperature and engine speed, with the RON test using a significantly lower (and variable) intake charge temperature and 600 revolutions per minute (rpm) engine speed, while the MON test is conducted at a much higher, fixed intake charge temperature and 900 rpm engine speed. Recent studies have demonstrated that in modern engines increasing MON at constant RON may actually lower the fuel knock resistance [6]. Octane sensitivity (S), the difference between RON and MON ($S = RON - MON$), can be interpreted as the sensitivity of the fuel autoignition kinetics to the temperature of the unburned end-gas [7]. Kalghatgi [8] and Mittal and co-workers [9] have shown that fuels with higher S have slower autoignition kinetics at lower temperatures than do fuels with lower S. They show that for modern engines, a more meaningful octane index (OI), compared to anti-knock index, is:

$$OI = RON - K \times S$$

(1)



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where K is a function of the temperature-pressure history that the fuel-air mixture experiences in the engine and is therefore different at different engine operating conditions. However, for specifying knock resistance in terms of OI , values of K at the most knock-limited low-speed, high-load conditions are most relevant. In boosted direct-injection spark-ignition (DISI) engines at low speed and high load, K is negative, consistent with the fact that fuels with higher octane sensitivity give higher knock resistance [10].

DISI engines can show substantially higher particulate matter (PM) emissions, on both a mass and particle number (PN) basis, compared to earlier technology port fuel injection engines [11, 12, 13, 14]. Because of the negative health impacts of fine particles [15] and the contribution of soot particles to global warming [16] regulatory agencies are putting into place large reductions in allowable levels of PM emissions for future model years [17, 18, 19]. Increased PM emissions from DISI engines are caused by diffusion combustion in locally rich regions. This can occur because of incomplete fuel spray breakup and evaporation, as well as impingement of the fuel spray on the piston or cylinder wall, and is made worse if substantial amounts of low volatility components are present in the fuel. Combustion then occurs as a diffusion flame or pool fire as the fuel evaporates with consequent production of soot [20,21].

For three-way catalyst equipped cars, the particles emitted at the tailpipe are 95% elemental carbon and consist almost entirely of accumulation mode particles (>30 nm) with an average diameter of about 70 nm [22,23]. It has also been noted that much higher levels of particles are generated during acceleration and cold-start operation as compared to steady-state. Therefore, for vehicle emission regulatory purposes steady-state test cycles are not appropriate. However, Aikawa and coworkers show very similar trends in fuel effects on PM emissions for transient and steady-state vehicle driving cycles [13]. Researchers at Honda have shown that for both port fuel injection and DI engines PM emissions are correlated with a particulate matter index (PMI) that can be calculated based on a detailed hydrocarbon analysis (DHA) for a gasoline. PMI is a function of the weight fraction, vapor pressure, and double bond equivalent (DBE) value for each component in the fuel [13,20]. Fuel components with high vapor pressure will evaporate quickly, minimizing diffusive, heterogeneous combustion or avoiding pool fire combustion if piston impingement occurs. The DBE is the number of hydrogen molecules required to saturate the double bonds and open rings present in a fuel molecule. A global survey of 1,445 gasoline samples showed a PMI range of 0.67 to 3.86 with a mean of approximately 1.6. A typical U.S. certification gasoline exhibits a PMI of 1.36 [13].

Ethanol produced from starch is the primary renewable fuel used in SI engines today, and ethanol may have several distinct advantages for application in DISI engines [24,25]. To achieve much larger quantities of biofuel with lower life-cycle greenhouse gas emissions, production must shift to lignocellulosic biomass feedstocks [26], which can be economically converted to ethanol [27]. Nevertheless ethanol is not without its disadvantages, including low volumetric energy content, high water solubility, and potential materials compatibility issues at high blend levels, all of which prevent it from being considered as a drop-in fuel. Thus, a large international

research effort is focused on converting lignocellulosic biomass into drop-in fuels, which are conventionally thought to be hydrocarbons. However, biomass typically contains 40 percent by weight (wt%) to 60 wt% oxygen, suggesting that conversion to hydrocarbons will be both technically and economically challenging. Analysis has shown that costs for hydrotreating of pyrolysis oil derived from biomass can exceed \$1 per gallon, with particularly high incremental costs for removal of the last increment of oxygen [28,29]. Gasoline boiling range oxygenates from partially upgraded biomass pyrolysis oils or made from biomass by acid or base-catalyzed deconstruction include phenolics, aryl ethers, and furans [30, 31, 32, 33, 34]. Additionally, isobutanol can be produced by fermentation of sugars, including cellulose-derived sugars [35]. Many of these oxygenates have high octane numbers and high energy density [36] and are thus desirable for enabling the deployment of more efficient DISI engines. The study reported here is part of an effort to determine the extent to which biomass oxygenates can function as drop-in fuels. We specifically focus on how the biomass-derived oxygenates ethanol, isobutanol, 2,5-dimethylfuran (DMF), anisole, 4-methylanisole (4-MA), 2,4-xyleneol, and 2-phenylethanol (2-PE) impact fuel properties, as well as knock-limited spark advance and PM emissions from a single cylinder DISI engine.

METHODS

Fuels and Fuel Property Measurements

The base gasoline was obtained from a local supplier, and oxygenates were obtained as reagent grade chemicals. p-Xylene (1,4-dimethylbenzene) and p-cymene (1-methyl, 4-isopropylbenzene) were used to increase the base gasoline RON and PMI without adding oxygen. Blends were prepared volumetrically at room temperature, and the blend concentration was confirmed by an in-house gas chromatography method.

DHA was performed by ASTM method D6729. Our implementation of this method via gas chromatography has been previously reported [37]. Once the components were identified and quantified by gas chromatograph, an Excel spreadsheet containing each component name and the percent by weight present was generated. Because a few hundred components were present, we eliminated those present at less than 0.05 wt%, which resulted in less than a 5% total reduction in sample. Heat of vaporization (HoV) was calculated from the DHA as previously described [37].

The actual blend concentration of ethanol was determined by ASTM method D5501. Ethanol blends are designated by Exx, representing the nominal volumetric ethanol concentration. Other oxygenates were measured by an in-house two-dimensional heart-cutting gas chromatography method that has been previously described [36].

PMI was calculated from the DHA as in Aikawa et al. [13]

$$PMI = \sum_{i=1}^n \left[\frac{(DBE_i + 1)}{VP(443K)_i} \times Wt_i \right] \quad (2)$$



where the double bond equivalent (DBE) of the individual compound is defined as:

$$DBE = (2C + 2 - H)/2 \quad (3)$$

W_i is the weight percent of each component, and VP is the vapor pressure at 443K. Vapor pressures at 443 K were estimated following the Lee and Kesler method [38].

$$P^{sat} = P_r^{sat} * P_c \quad (4)$$

$$\ln P_r^{sat} = (\ln P_r^{sat})^{(0)} + \omega (\ln P_r^{sat})^{(1)} \quad (5)$$

$$(\ln P_r^{sat})^{(0)} = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \ln T_r + 0.169347 T_r^6 \quad (6)$$

$$(\ln P_r^{sat})^{(1)} = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \ln T_r + 0.43577 T_r^6 \quad (7)$$

where P^{sat} is the vapor pressure at a desired temperature, T_r is the reduced temperature (desired temperature/critical temperature), P_c is the critical pressure, and ω is the acentric factor. Critical properties for individual compounds were taken from literature sources [39,40].

Single-Cylinder Engine Experiments

The single-cylinder engine specifications are shown in Table 1. This engine was developed from a 2009 model year GM Ecotec 2.0 L LNF-series engine, with a wall-guided DI combustion system. The dynamometer, engine control, air handling, fuel supply, and combustion analysis systems have all been previously described [23]. A standard procedure for purging the fuel system and running the engine at a high power for a set period of time was performed before testing each new fuel.

Table 1. Single-cylinder engine specifications.

Displacement (L)	0.5
Bore (mm)	86.0
Stroke (mm)	86.0
Connecting rod length (mm)	145.5
Compression ratio	9.2
Number of valves	4
Combustion System	Wall-guided Direct Injection

For spark timing sweep experiments, a relatively low engine speed was used because longer combustion duration increases exposure of the unburned end-gas to heat and pressure making the engine more sensitive to autoignition and knock. Experimental conditions were a

nominal load of 925 kPa net mean effective pressure (NMEP), 1,500 rpm, and intake air temperature of 35°C (measured at the intake port). The load and intake air temperature were selected to ensure the engine could operate on the 88 RON hydrocarbon base gasoline. Cam phasing, fuel pressure, and start of injection were based on GM calibration data for this speed and load (see Table 2). Spark timing was initially set to 10 crank angle degrees (CAD) before top dead center (BTDC), fuel and air flows were adjusted slightly lean (0.3% - 0.5% oxygen in the exhaust gas). For each spark sweep the fuel and air flows were held constant after achieving the nominal 925 kPa NMEP load at 10° BTDC spark advance. Absolute fueling rates were unique to each blend because of energy and gravimetric density differences. Spark was then advanced in one or two degree increments. The engine output (load) increased up to minimum advance for best torque (MBT) because combustion phasing becomes optimal there.

Maximum pressure rise rate (MPRR) was used as a real-time measure of impending or actual knock, and spark timing was advanced until any cycle during the 100-cycle data collection period exceeded 1,100 kPa/CAD (the programmed limit triggering automatic spark retard). It should be noted that this MPRR limit turned out to be too aggressive (strong knock) and is not to be mistaken as a recommended practice. Integrated knock, or knock-integral (KI) was calculated by first filtering the in-cylinder pressure signal using a second-order Butterworth band-pass filter (5 - 15 kHz band), then rectifying the filtered signal [41]. A knock window was selected starting at 5° after top dead center and lasting for 30°. A reference window was selected starting at 210° BTDC and 30° duration. The filtered, rectified signal was then integrated separately over both the knock and reference windows. The KI value is defined by:

$$KI = \int_{Knock} / \int_{Reference} - Threshold \quad (8)$$

The threshold value chosen for this study was 0.5 KI units.

Table 2. Engine operating parameters.

Engine Speed/Load (rpm/kPa)	2,500/ 1,300	2,000/ 300	1,500/ 600	1,500/ 925 @ start of spark sweep
Intake Press (bar abs)	1.15	0.46	0.70	0.86
Intake Temp (°C)	35	35	35	35
Fuel Rail Pressure (bar)	68	35	68	68
Start of Injection (°BTDC)	300	265	270	290
Spark Timing (°BTDC)	10	28	28	10, sweep starting point
Intake Cam Phasing (CAD) ^a	30	30	35	40
Exhaust Cam Phasing (CAD) ^b	20	25	30	35
Coolant / Oil Temp (°C)	85 / 90			
Equivalence Ratio	0.98			

^aCAD advanced from full retard. ^bCAD retarded from full advance.

Three separate engine speed and load operating points were used to evaluate fuel effects on PM-mass and PN emissions. These were 2,500 rpm-1,300 kPa NMEP; 2,000 rpm-300 kPa NMEP; and 1,500 rpm-600 kPa NMEP. Engine operating parameters for the PM experiments are shown in Table 2. The engine was operated slightly lean to ensure repeatable PM measurements, i.e., stoichiometric operation produced large PM measurement variations from minor air-fuel ratio instabilities. PM-mass, PN, and engine data were recorded for 1 minute at 1 Hz and then averaged. Each engine operating point was run several times in a randomized order across several days for each fuel.

The PN emission measurement system consists of a Dekati FPS-4000 two-stage exhaust sample dilution system upstream of a Dekati Thermodenuder feeding the diluted sample to a TSI Fast Mobility Particle Sizer (FMPS) model 3091. The Dekati dilution system uses a primary perforated wall flow type dilutor with dilution air that is temperature controlled (set to 150°C). The secondary stage of the dilutor is an ejector dilutor that uses room temperature dilution air and acts as the main driving force for the diluted exhaust sample flow. The overall dilution ratio was set to between 25:1 and 30:1 for all of the testing in this study. The Dekati Thermodenuder operating temperature was 275°C. The TSI FMPS measures PN distribution for particle diameters between 5.6 to 560 nm with a 32-channel resolution. The Thermodenuder is intended to remove all volatile compounds, so that the resulting FMPS measurements are theoretically on a strictly elemental carbon emissions basis. This sample processing was done because studies have shown that DISI engine vehicles equipped with a three-way exhaust catalyst emit primarily elemental carbon PM [22]. Separately, an AVL Micro-Soot Sensor (MSS) is connected to the raw engine exhaust and measures real-time PM-mass. The MSS includes contains its own built in dilution system, which was nominally set to an 8:1 ratio.

RESULTS AND DISCUSSION

Fuel Properties

The properties of the gasoline base fuel have been reported previously [37], but are reproduced here for completeness. Compound classes and other properties of the base gasoline derived from the DHA are shown in Table 3. The base gasoline was a sub-octane blendstock for oxygenate blending intended for summertime use in an ozone non-attainment area. Particle emissions and PMI will be affected by aromatic and olefin content, and these values are in the middle range for U.S. gasoline [42].

Net heating values and boiling points for the oxygenates examined are shown in Figure 1, and other properties are listed in Table 4. The high boiling points of 2-PE and 2,4-xylene relative to the gasoline end point limit of 225°C are notable, as are the high volumetric energy densities of several of the oxygenates relative to conventional gasoline. All exhibit high octane number. The blending RON and MON values are reported in Table 4 because some of the compounds' volatilities are too low to have their RON and MON measured

directly. However, it must be noted that blending RON and blending MON cannot be considered absolute values because they depend on the chemistry of the base fuel and blending level. Furthermore, any errors in the octane numbers and concentration measurements are amplified by the equation for calculating these blending octane numbers, especially at low blending levels. For example, at the 20 vol% blend level, blending octane number can be computed as:

$$\text{Blending Octane Number} = [(\text{Blend ON}) - (0.8) * (\text{Base Fuel ON})] / 0.2 \quad (9)$$

In this example, division by the volume fraction 0.2 results in a fivefold increase in error of the measured quantities in the resulting blending octane number.

Table 3. PIANO analysis and other properties of the base gasoline.

Paraffins	D6729	vol%	11.5
Isoparaffins	D6729	vol%	47.9
Aromatics	D6729	vol%	23.7
Naphthenes	D6729	vol%	7.8
Olefins	D6729	vol%	8.4
Average MW	D6729	g/mol	95.9
Carbon	D6729	wt%	86.1
Hydrogen	D6729	wt%	13.9
Density at 15°C	D4052	g/ml	0.7374
Dry vapor pressure equivalent (Reid vapor pressure equivalent)	D5191	Psi	6.86
Distillation T ₁₀	D86	°C	61
Distillation T ₅₀	D86	°C	98
Distillation T ₉₀	D86	°C	154
Final Boiling Point	D86	°C	198

PIANO = paraffins, isoparaffins, aromatics, naphthenes, and olefins

Ethanol and isobutanol have high vapor pressure at 443 K and a DBE value of zero, so do not cause PMI to increase. DMF has a relatively high vapor pressure but a DBE of 3 and would be expected to moderately increase PMI. Anisole, 4-MA, 2,4-xylene, and 2-PE have much lower vapor pressures at 443 K and have DBEs of 4, causing PMI to increase. These expectations are met as shown in Table 5, which presents properties of the gasoline blendstock-oxygenate blends. Blends were also prepared with p-xylene (20 vol%) and p-cymene (20 vol%) to demonstrate the impacts of increasing aromatic content without fuel oxygen. The Sunoco GTX demonstrates that high aromatic content (45.5 vol%) can be offset by high vapor pressure at 443 K (note low T₉₀) resulting in a low PMI fuel. Distillation curves of selected fuels are shown in Figure 2. Blending with 20 vol% 2-PE causes the gasoline to fail the maximum limit for T₉₀ and nearly fail for T₅₀. The 10 vol% 2,4-xylene blend nearly fails T₉₀, and the 21% 4-MA blend nearly fails T₅₀. The relatively high boiling point of these oxygenates significantly limits levels that can be blended into ASTM D4814-compliant gasoline.