ORNL/TM-2016/42

Summary of High-Octane, Mid-Level Ethanol Blends Study

July 2016

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE US DEPARTMENT OF ENERGY

DOCUMENT AVAILABILITY

Reports produced after January 1, 1996, are generally available free via US Department of Energy (DOE) SciTech Connect.

Website http://www.osti.gov/scitech/

Reports produced before January 1, 1996, may be purchased by members of the public from the following source:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone 703-605-6000 (1-800-553-6847)
TDD 703-487-4639
Fax 703-605-6900
E-mail info@ntis.gov
Website http://www.ntis.gov/help/ordermethods.aspx

Reports are available to DOE employees, DOE contractors, Energy Technology Data Exchange representatives, and International Nuclear Information System representatives from the following source:

Office of Scientific and Technical Information
PO Box 62
Oak Ridge, TN 37831
Telephone 865-576-8401
Fax 865-576-5728
E-mail reports@osti.gov
Website http://www.osti.gov/contact.html

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ORNL/TM-2016/42

Bioenergy Technologies Program

Summary of High-Octane Mid-Level Ethanol Blends Study

Tim Theiss, ORNL
Teresa Alleman, NREL
Aaron Brooker, NREL
Amgad Elgowainy, ANL
Gina Fioroni, NREL
Jeongwoo Han, ANL
Shean Huff, ORNL
Caley Johnson, NREL
Mike Kass, ORNL
Paul Leiby, ORNL
Rocio Uria Martinez, ORNL
Robert McCormick, NREL
Kristi Moriarty, NREL
Emily Newes, NREL
Gdadebo Oladosu, ORNL
James Szybist, ORNL
John Thomas, ORNL
Michael Wang, ANL
Brian West, ORNL

Date Published: July 2016

Prepared by
OAK RIDGE NATIONAL LABORATORY (ORNL),
NATIONAL RENEWABLE ENERGY LABORATORY (NREL), and
ARGONNE NATIONAL LABORATORY (ANL)

Oak Ridge, TN 37831-6283
managed by
UT-BATTELLE, LLC
for the
US DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

CONTENTS

Page

LIST OF FIGURES

ACKNOWLEDGEMENTS

This report and the work described were sponsored by the U.S. Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy's (EERE's) Bioenergy Technologies Office. The authors gratefully acknowledge the support and direction of Alicia Lindauer of that office. This work has also benefited from input, direction, and support from numerous peers within industry, the DOE Vehicle Technologies Office, and the U.S. Environmental Protection Agency. The authors also acknowledge and appreciate the thorough review from Scott Sluder at ORNL.

The authors are indebted to many technical experts in industry and government. While these experts provided valuable guidance and information as noted above, this consultation does not constitute endorsement by their organizations of either the study or the results.

ACRONYMS

ADOPT	Automotive Deployment Options Projection Tool
AKI	anti-knock index
ANL	Argonne National Laboratory
BOB	blendstock for oxygenate blending
CO_2e	GHG equivalent emissions deemed as CO_2 and often in mass units
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
E0	gasoline with no ethanol content
E10	gasoline with 10% ethanol
E85	also known as flex fuel, gasoline blended with 51-83% ethanol
Ex	other ethanol/gasoline mixtures with x% ethanol, such as E15, E25, E30, E40, E50
ETW	equivalent test weight
FFV	flexible-fuel vehicle
GHG	greenhouse gas
GM	General Motors Company
GREET	Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation Model
HFET	Highway Fuel Economy Test
HOF	high octane fuel
KLSA	knock limited spark advance
LP	linear programming
MON	motor octane number
NREL	National Renewable Energy Laboratory
OEM	original equipment manufacturer
ORNL	Oak Ridge National Laboratory
RVP	Reid vapor pressure
RFS	Renewable Fuel Standard
RON	research octane number
SI	spark ignition
SUV	sport utility vehicle
UST	underground storage tank
US06	EPA US06 high-load, high-speed aggressive test cycle, part of the EPA Supplemental Federal Test Procedure (SFTP)
V6	V-six engine cylinder configuration
V8	V-eight engine cylinder configuration
WTW	well-to-wheels

BACKGROUND

Original equipment manufacturers (OEMs) of light-duty vehicles are pursuing a broad portfolio of technologies to reduce CO_2 emissions and improve fuel economy. Central to this effort is higher efficiency spark ignition (SI) engines, including technologies reliant on higher compression ratios and fuels with improved anti-knock properties, such as gasoline with significantly increased octane numbers. Ethanol has an inherently high octane number and would be an ideal octane booster for lower-octane petroleum blendstocks. In fact, recently published data from Department of Energy (DOE) national laboratories (Splitter and Szybist, 2014a, 2014b; Szybist, 2010; Szybist and West, 2013) and OEMs (Anderson, 2013) and discussions with the U.S. Environmental Protection Agency (EPA) suggest the potential of a new high octane fuel (HOF) with 25–40 vol % of ethanol to assist in reaching Renewable Fuel Standard (RFS2) and greenhouse gas (GHG) emissions goals. This mid-level ethanol content fuel, with a research octane number (RON) of about 100, appears to enable efficiency improvements in a suitably calibrated and designed engine/vehicle system that are sufficient to offset its lower energy density (Jung, 2013; Thomas, et al, 2015). This efficiency improvement would offset the tank mileage (range) loss typically seen for ethanol blends in conventional gasoline and flexible-fuel vehicles (FFVs). The prospects for such a fuel are additionally attractive because it can be used legally in over 18 million FFVs currently on the road. Thus the legacy FFV fleet can serve as a bridge by providing a market for the new fuel immediately, so that future vehicles will have improved efficiency as the new fuel becomes widespread. In this way, HOF can simultaneously help improve fuel economy while expanding the ethanol market in the United States via a growing market for an ethanol blend higher than E10.

The DOE Bioenergy Technologies Office initiated a collaborative research program between Oak Ridge National Laboratory (ORNL), the National Renewable Energy Laboratory (NREL), and Argonne National Laboratory (ANL) to investigate HOF in late 2013. The program objective was to provide a quantitative picture of the barriers to adoption of HOF and the highly efficient vehicles it enables, and to quantify the potential environmental and economic benefits of the technology. The project consisted of the following interconnected efforts.

- Develop a preliminary description of the key knock resistance properties of HOF to obtain a full understanding of both regulatory and ASTM standard development issues with regard to defining and introducing this fuel.

- Experimentally validate and measure the efficiency and performance benefits of HOF in a dedicated vehicle. This vehicle-level demonstration complements ongoing engine-based studies researching the benefits of increased fuel octane and engine compression ratio.

- Experimentally validate and measure the performance benefits of HOF in current FFVs. Demonstrating a performance benefit in legacy FFVs could help in marketing ethanol blends for the legacy FFV fleet, which could bolster development of the infrastructure for fueling future vehicles specifically designed for this fuel.

- Study the impacts on the petroleum refining sector and life-cycle GHG benefits across the US economy that would occur through broad adoption of HOF and the highly efficient vehicles it will enable. This effort is supported by analysis results under other subtasks:

  - Ascertain the shares of HOF and non-HOF demand of the light-duty vehicle fleet. These shares determine the refinery operations and the gasoline components in the refinery linear programming (LP) models.

  - Define fuel property requirements for HOF. These constrain the properties of the hydrocarbon blendstock, which can have a large effect on life-cycle energy use and GHG emissions.

- Gain a broad understanding of economic and regulatory barriers to adoption of HOF by four key stakeholder groups: fuel producers/distributors, fuel retailers, vehicle manufacturers, and consumers. Each group is subject to different federal and state regulatory requirements and has different economic constraints.

- Determine the extent to which existing station and terminal infrastructure is compatible with HOF-range (25 to 40%) ethanol blends, whether infrastructure components are compatible, and whether there is a blend-level breakpoint at which infrastructure compatibility is less of an obstacle.

- Evaluate the cost reduction potential of HOF blendstocks including natural gasoline which has been suggested as a possible low-cost blendstock for HOF.

ENGINES AND KNOCK

A major efficiency-limiting combustion phenomenon in SI engines is referred to as knock or more specifically end-gas knock. Desired cylinder combustion events are initiated at the proper time by the spark which ignites the surrounding air-fuel mixture. A flame zone then expands, propagating through the combustion chamber, ideally consuming all the fuel, releasing heat and causing a pressure rise that imparts force on the moving piston. Most of the force increase is applied to the piston during the expansion stroke such that the combustion process creates useful mechanical work. As the spark-initiated flame zone expands, the unburned mixture beyond the flame zone is increasing in temperature and pressure due both to the expanding gas in the flame zone and the piston compressing the mixture further. Knock occurs when this unburned fuel-air mixture, known as the end-gas, detonates, or burns very rapidly essentially by compression ignition. This undesirable event is also referred to as autoignition of the air-fuel mixture. A knock event applies sudden forceful pressure waves to the piston, piston rings and other components. Knock must be limited due to the potential for significant engine damage. There is typically an efficiency penalty for operating strategies that mitigate knock, including delayed spark timing and operating the engine fuel-rich.

Manufacturers are building vehicles with smaller turbocharged engines (downsizing) and with powertrain controls aimed at lowering engine speed (downspeeding). Downspeeding and downsizing of SI engines can promote improved efficiency because these engines are typically more efficient at lower speeds and higher loads. However, engines operating at these conditions are more prone to engine knock; mitigating knock through adjustment of spark timing and/or fuel enrichment is done at the expense of efficiency. When an engine at a given speed point is commanded to increase load such that knock will begin, the controller will “retard” the spark timing to later in the cycle than would otherwise be optimum for efficiency and power. This spark timing change prevents end-gas knock and is known as knock limited spark advance (KLSA) and some efficiency is lost to avoid knock. At higher loads, the use of further spark retarding can reach a limit (due to excessively high exhaust temperature, for example) and fuel enrichment is also used to meet the load while avoiding knock and engine damaging exhaust temperatures. Enrichment further decreases efficiency and also increases emissions.

The opportunity for further downsizing and downspeeding of engines to improve fuel economy is limited by the available octane rating of fuels. Note that higher octane fuels will allow higher efficiency designs of naturally aspirated and turbocharged engines dedicated to use the high octane fuel.

KNOCK RESISTANCE OF ETHANOL-GASOLINE BLENDS

The tendency of an SI engine fuel to resist auto-ignition and engine knock is measured as the octane number, a critical performance parameter for SI engines. In the United States, the octane number at the retail pump is given as the anti-knock index (AKI), the average of the RON and the motor octane number (MON), AKI = ½(RON + MON). The differences between the RON and MON test methods are fuel-air charge temperature and engine speed; RON testing uses a comparatively low fuel-air charge temperature and slower engine speed, whereas the MON test is conducted at a significantly higher fuel-air charge temperature and faster engine speed. For modern light-duty SI engines, knock resistance is known to be well correlated with RON.

Given the high RON of ethanol (109), it is commonly blended into a sub-octane blendstock for oxygenate blending (BOB) having a RON of approximately 84 to 88 to produce finished gasoline having adequate knock resistance (in terms of the anti-knock index). Ethanol has a nonlinear effect on the RON of the finished blend, with a diminishing effect as the ethanol content is increased. The increase in RON depends on the starting RON of the BOB, but it increases to around 100 to 105 at E50. With addition of ethanol, the typical 87 AKI E10 can produce a 99-100 RON E25.

Fuel knock resistance for direct injection engines is enhanced by the fact that the fuel-air charge is cooled in the cylinder as the fuel evaporates, reducing the end-gas temperature. This is a major advantage of direct injection over other SI engine fuel system types and is important regardless of the fuel type or the octane number. However, at 25°C, the heat of vaporization of gasoline boiling-range hydrocarbons is 350 to 400 kJ/kg, while that of ethanol is 924 kJ/kg. The heat of vaporization difference is even greater when based on a mass stoichiometric mixture basis, in which the value for hydrocarbon is 22 kJ/kg while that for ethanol is 92 kJ/kg.

An objective in the HOF project was to develop a clear understanding of how to measure heat of vaporization and how to quantify knock resistance for ethanol-gasoline blends. Blends of ethanol at nominal 10, 20, 25, 30, 40, and 50 vol % were prepared with three gasoline blendstocks and a natural gasoline. Natural gasoline, also known as natural gas condensate, is an inexpensive byproduct of natural gas production. Consisting primarily of pentanes, it has low octane number, and is very volatile. Because ethanol is such a potent octane booster, especially with lower octane blendstocks, natural gasoline blends were included in this study.

Heat of vaporization was measured by two methods developed under the project: by differential scanning calorimetry/thermogravimetric analysis and as estimated from detailed hydrocarbon analysis. A striking feature of the results was the insensitivity of the heat of vaporization to hydrocarbon blendstock for temperatures up to 150°C: all four hydrocarbon blendstocks tested had essentially the same heat of vaporization in kJ/kg and the same response to blending with ethanol (Figure 1). These results have been published in a peer-reviewed journal (Chupka, 2015).

The base gasoline and ethanol blends were evaluated in a single-cylinder engine developed from a 2009 model year GM Ecotec 2.0 liter LNF-series engine with a wall-guided direct-injection combustion system. Knock-limited spark advance was measured in spark timing sweep experiments at a nominal load of 925 kPa net mean effective pressure, 1500 rpm, and an intake air temperature of 35°C (measured at the intake port). A relatively low engine speed was used because a longer combustion duration increases exposure of the unburned end-gas to heat and pressure, making the engine more sensitive to autoignition and knock. The load and intake air temperature were selected to ensure the engine could operate on the 88 RON hydrocarbon base gasoline. A plot of KLSA versus RON is shown in Figure 2, which shows that for heats of vaporization ranging from 353 to 527 kJ/kg, RON is an excellent predictor of KLSA under these engine operating conditions.

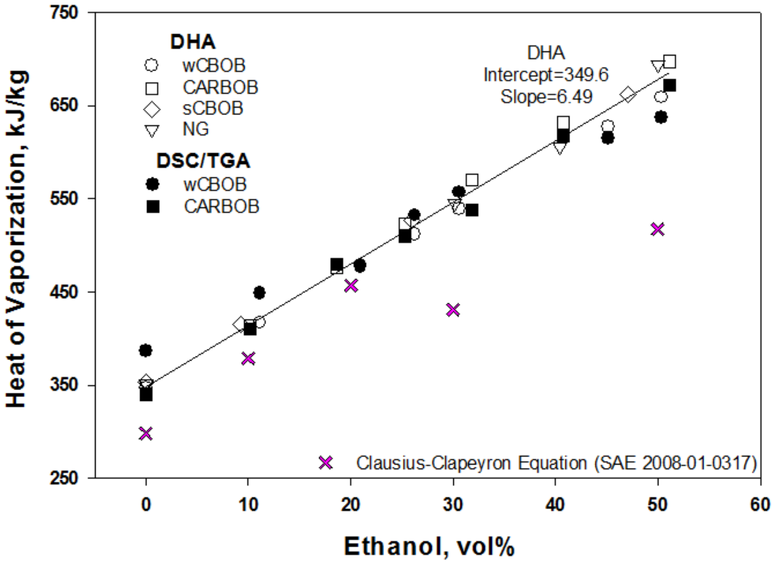

Figure 1. Heat of vaporization as a function of ethanol content measured by differential scanning calorimetry/thermogravimetric analysis (California Reformulated Gasoline Blendstock for Oxygenate Blending blends) at 23°C and by detailed hydrocarbon analysis (all blends) at 25°C.

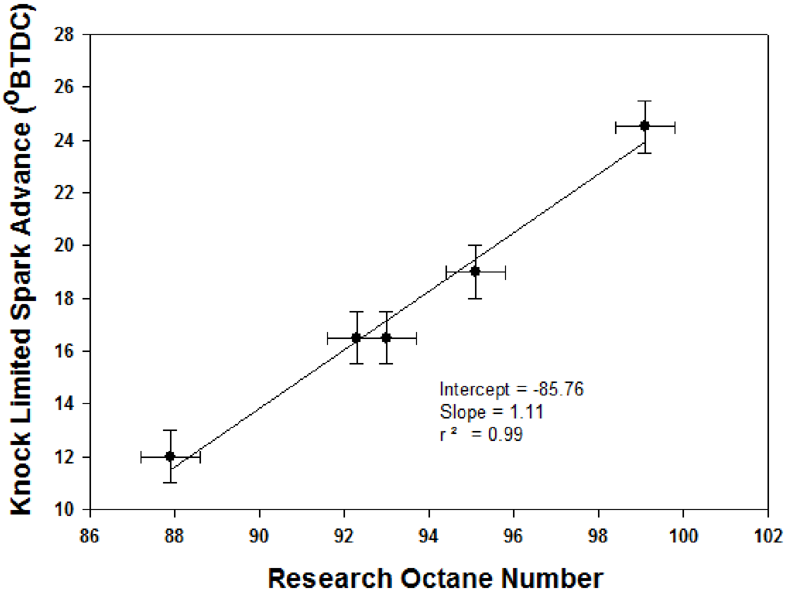

Figure 2. KLSA versus RON. The E50 blend is not included because KLSA could not be reached at the test load.

The results demonstrate that under relatively moderate load conditions in current-technology engines, heat of vaporization is not a factor in engine knock resistance. However, under more extreme conditions enabled by boosted engines using large amounts of spark timing retard to control knock, heat of vaporization may play a role. Additionally, it may be possible to calibrate future high-efficiency engines to take advantage of the heat of vaporization by, for example, injecting a fraction of the fuel after the intake valve closes. These results and associated discussion have been published (Sluder et al, 2016) and the possibilities are being examined under ongoing DOE-sponsored research.

EFFECTS OF HIGH OCTANE FUEL IN A DEDICATED VEHICLE

It is essential to demonstrate the benefits a HOF paired with powertrains optimized for efficiency by taking full advantage of this fuel's properties. To demonstrate the potential efficiency and fuel economy benefits of high-octane mid-level ethanol blends in a dedicated vehicle, a Cadillac ATS equipped with a 2.0 liter turbocharged, direct-injection engine and manual transmission was acquired. A test plan was developed to explore HOF powertrain optimization using this vehicle as a platform; first with the vehicle in unaltered form and then with a series of physical modifications to the engine and vehicle combined with using chassis dynamometer settings to experimentally simulate alternative vehicle configurations.

To downspeed the engine in the ATS vehicle, larger-diameter drive wheels were procured. In addition, with support from General Motors (GM), a custom 2.85:1 differential was acquired to replace the factory 3.27:1 gear set to further downspeed the system. The combination of the larger drive wheels and 2.85 gear set lowered the engine speed by 20%. GM also provided an instrumented cylinder head to permit measurement of cylinder pressure and combustion phasing, and a nondisclosure agreement was executed to permit sharing of a proprietary engine calibration tool.

In the first phase of the research, the factory compression ratio of 9.5:1 was used for baseline experiments with fuels ranging from 87.5 AKI (91 RON) to 101 RON and ethanol levels ranging from 0 to 30%. In the second phase of experiments, the factory compression ratio was retained while downspeeding was implemented with the aforementioned tires and differential. Additionally, downsizing was effectively achieved by evaluating the vehicle at an increased test weight and increased road load forces, simulating installation of the 2.0 liter engine in a mid-size 4,750 pound sport utility vehicle (SUV).

Fuel economy improvements with HOF were demonstrated with the factory pistons along with downspeeding and downsizing, which forces the engine to operate at higher loads. The engine is more knock-prone under these conditions, and increasing the octane level through the addition of ethanol allows more efficient combustion phasing. Figure 3 shows the gasoline equivalent fuel economy for the Cadillac ATS on the high-load US06 cycle for both the stock setup and the downsped condition. The US06 test requires high engine loads and thus causes the engine controller to retard the ignition timing to suppress knock. Therefore, increasing the octane level allows for improved combustion phasing and improved fuel economy, even in the stock condition. Downspeeding the engine requires even higher loads, which would be expected to further exacerbate knock. As shown in Figure 3, the high octane E30 yielded an efficiency improvement of more than 5% over the 88 AKI E10 in the stock setup. Downspeeding improved fuel economy with all fuels relative to the stock condition. Most notable is that a 10% efficiency improvement was demonstrated on this cycle with high-octane E30 in the downsped condition compared with the stock condition with regular E10. Note that in Figures 3, 4 and 5 the fuel economy (E0 MPGeq) represents miles per gallon normalized to the 97 RON E0 (93 AKI) fuel based on lower (volumetric) heating value.

Similar results for the Highway Fuel Economy Test (HFET) are shown in Figure 4. The HFET is a fairly light load test with mild accelerations, an average speed of 48 mph, and a top speed of only 60 mph. For most vehicles, the HFET is not a knock-limited cycle; however, with extreme downspeeding, the ATS is apparently knock-limited with the 88 AKI E10 so that the HOF allows for improved efficiency.

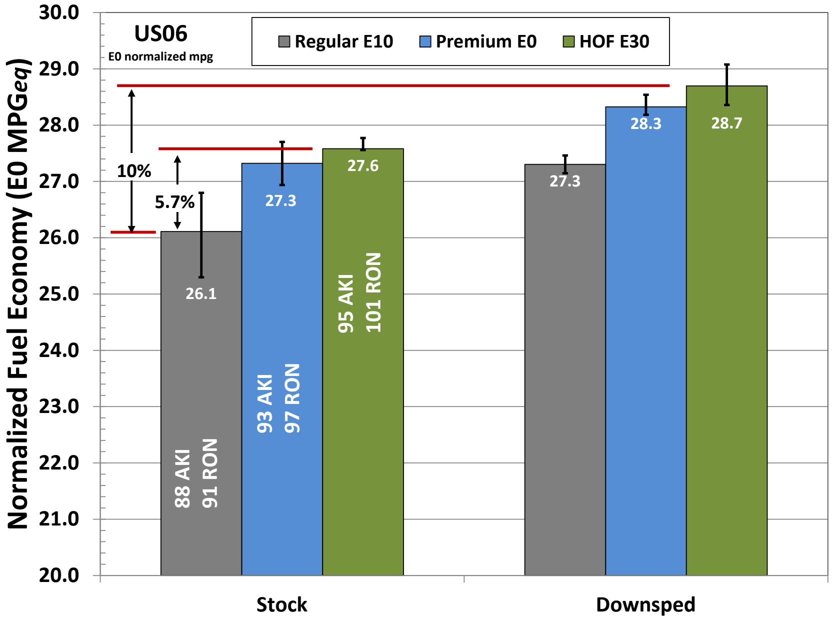

Figure 3. Gasoline equivalent fuel economy for a Cadillac ATS on high-load US06 cycle for stock and downsped conditions with three fuels. Range bars indicate maximum and minimum results for multiple tests.

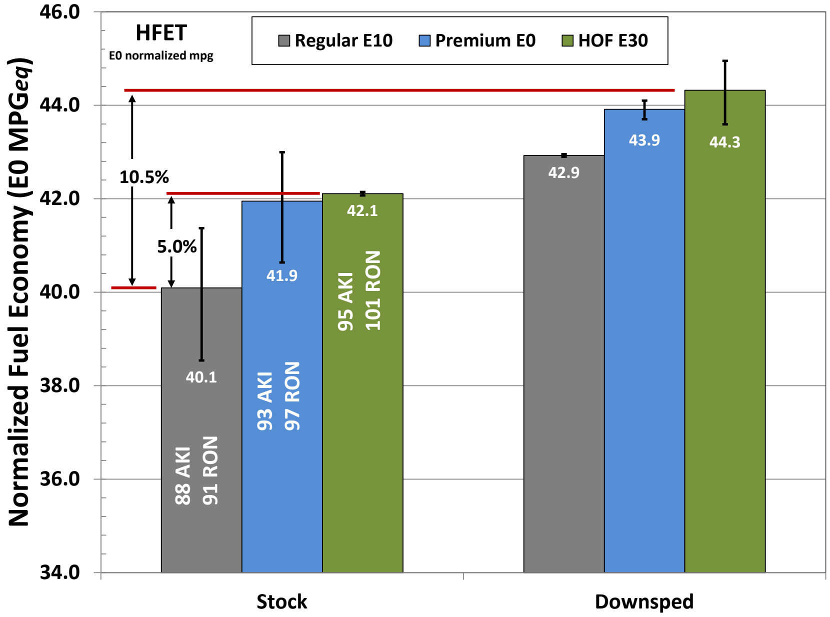

Figure 4. Gasoline equivalent fuel economy for a Cadillac ATS on the Highway Fuel Economy test for stock and downsped conditions with three fuels. Range bars indicate maximum and minimum results for multiple tests.

The Cadillac ATS equivalent test weight (ETW) is 3,750 pounds. Setting the vehicle dynamometer to simulate a Cadillac SRX SUV with a 4,750 ETW and higher road load further loaded the engine, essentially simulating installing the 2.0 liter ATS powertrain in a larger SUV. In these downsped/downsized experiments, the high-octane E30 yielded a 4% efficiency improvement over the regular E10 on the HFET and more than a 10% improvement over the certification database fuel economy for the same vehicle equipped with a naturally-aspirated V6 (Figure 5).

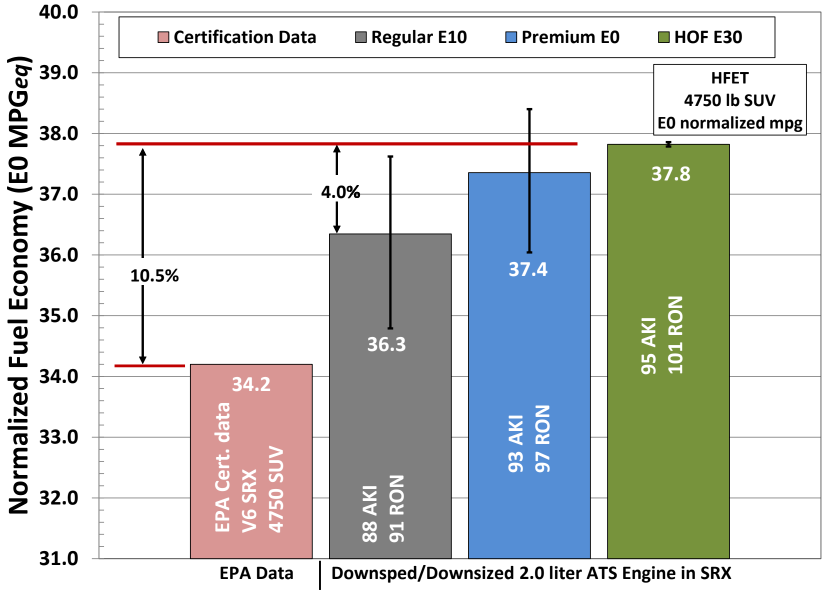

Figure 5. Highway fuel economy test results for downsped/downsized case. EPA certification data for a Cadillac SRX V6 are shown for comparison. Range bars indicate maximum and minimum results for multiple tests.

In phase 3 of the effort, the 10.5:1 compression ratio pistons were installed in the engine. These custom pistons were iteratively designed by KS Kolbenschmidt GMBH, and static and dynamic engine models were exercised by GM to ensure there would be no mechanical interference between the custom pistons and the cylinder head or valves. Following design approval by GM, custom 10.5:1 and 11:1 pistons were fabricated. Upon installation of the 10.5:1 pistons, the engine ran normally for a short time; but engine problems (unrelated to the pistons) precluded completion of the high-compression experiments before publication of this summary report.

EFFECTS OF HIGH OCTANE FUEL ON LEGACY VEHICLES

A small pilot study was conducted to explore the potential performance benefits of high octane ethanol blends in the legacy fleet (Thomas, et al., 2015). There are more than 18 million FFVs currently on the road in the United States, vehicles capable of using any gasoline/ethanol blend from E0 to E85. If currently available FFVs can realize a performance advantage with a high octane ethanol blend such as E25 or E30, then perhaps consumer demand for this fuel can serve as a bridge to future dedicated vehicles. Experiments were performed with four FFVs using a 10% ethanol fuel (E10) with 88 AKI, and a market gasoline blended with ethanol to make a 30% by volume ethanol fuel (E30) with 94 AKI. The RONs were 92.4 for the E10 fuel and 100.7 for the E30. General Motors (GM), Ford and Chrysler have produced the vast majority of FFVs on the road; GM has produced over half of these. Thus two GM vehicles and one each from Ford and Chrysler were recruited for the study, including

- 2014 GMC Sierra pickup truck, 4.3 liter V6 direct-injection engine
- 2014 Chevrolet Impala, 3.6 liter V6 direct-injection engine
- 2013 Ford F150 pickup truck, 5.0 liter V8 port-fuel injected (PFI) engine
- 2013 Dodge minivan, 3.6 liter V6 PFI engine

All four vehicles were naturally-aspirated; the two GM vehicles had gasoline direct-injection engines and the Ford and Dodge vehicles featured port fuel injection. Significant wide-open-throttle performance improvements were measured for three of the four FFVs running the high-octane E30 blend, with one vehicle showing no change. The most significant performance benefit was noted on the GMC Sierra FFV, as shown in Figure 6. This performance gain was noted to be comparable to that for a similar Chevrolet Silverado tested with E85 (*Car and Driver*, 2014). Consistent with expectations, fuel economy measurements over the standard city and highway certification cycles tracked the energy density of the test fuels, indicating insignificant knock-limited operation with the E10 base fuel on these light load cycles.

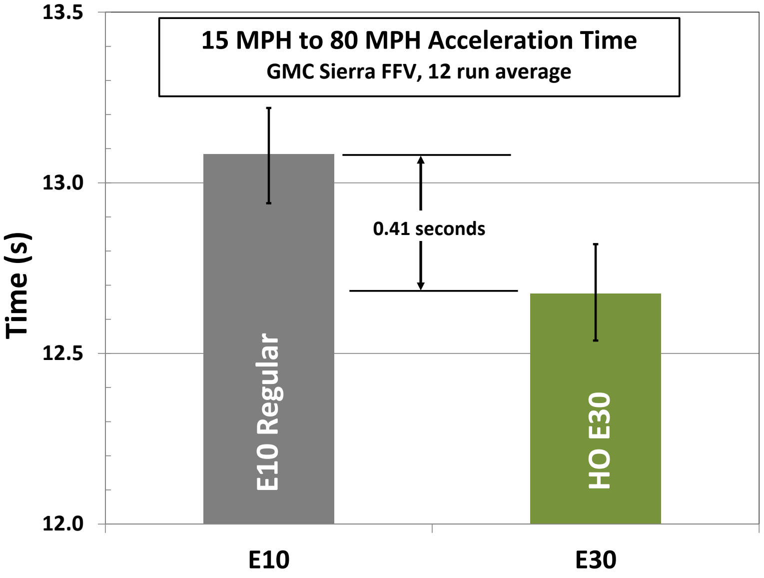

Figure 6. Acceleration time for GMC Sierra FFV using regular E10 and high octane E30 fuel. Range bars show maximum and minimum for 12 tests.

Experiments with a 2014 Ford Fiesta (non-FFV) vehicle with a small turbocharged direct-injection engine were conducted with a regular grade of gasoline without ethanol (E0) and a splash blend of this same fuel with 15% ethanol by volume (E15). The addition of 15% ethanol increased the RON from 90.7 for the E0 to 97.8 for E15. Significant improvements in wide-open-throttle and thermal efficiency performance were measured for this vehicle when fueled with the high-octane E15. It achieved near volumetric fuel economy parity on the aggressive US06 drive cycle, demonstrating the potential for improved fuel economy in forthcoming downsized, downsped engines with HOF.

Figure 7 compares E15 fuel economy on a relative basis with E0 performance in the Ford Fiesta to highlight the improved efficiency for high-octane E15 despite the lower heating value. The expected drop in miles per gallon is 5.6% for E15 versus E0 (based on volumetric energy density ratio), and is denoted by the horizontal red line in the figure. Note that the E15 fuel economy was considerably higher for all tests. For the US06 cycle, volumetric fuel economy parity was almost realized with E15, indicating a 4.6% improvement in thermal efficiency. These results were due to the apparent knock-limited operation on the high-load US06 cycle for this small, turbocharged engine. HOF enables less spark retard and significantly improved efficiency. These results are consistent with those reported by others with turbocharged, direct-injection engines (Jung, 2013; Leone, 2014). Note that the energy density difference between E0 and E15 is very similar to that expected between E10 and E25. Note also that no changes were made to the Fiesta's shift schedule. Hardware and software changes to future vehicles using high-octane mid-level blends would be expected to enable greater efficiency gains from downspeeding. It is important to note that the results for this EcoBoost Fiesta are not representative of what might be expected from the majority of legacy or current production vehicles.

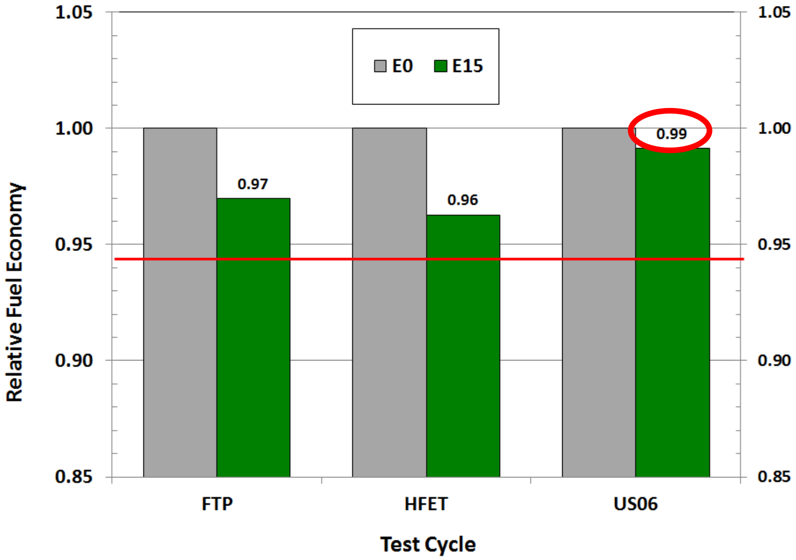

Figure 7. Relative fuel economy for regular E0 and high-octane E15 fuel in a Ford Fiesta. The red line indicates the expected fuel economy with E15 based on the volumetric heating value ratio of the fuel.

Results of vehicle experiments in this program indicate the following:

- High-octane mid-level ethanol blends improved the acceleration performance of legacy FFVs.
- HOF can improve the efficiency of vehicles equipped with turbocharged, direct-injection engines by more than 5%.
  - Efficiency improvements of 5% allow for “volumetric fuel economy parity”; that is, the efficiency gain in future HOF vehicles fueled with E25 would essentially return the same fuel economy as in comparable present-day vehicles fueled with regular E10, despite the lower energy density associated with higher ethanol blending.

WELL-TO-WHEELS GREENHOUSE GAS EMISSIONS ANALYSIS OF HOF

The objective of the well-to-wheels (WTW) analysis is to model petroleum refining to produce RON 100 final gasoline products with a range of ethanol blending levels and gasoline blendstocks . Such blendstocks matched to these different levels of ethanol require different petroleum refining operations during production (Hirshfeld, 2014). Addressing these various blending options is especially important given that US refineries may face the increased use of both heavy crudes, such as oil from the Canadian oil sands, and very light crude shale oil from shale formations such as Bakken and Eagle Ford, and the predicted changeover in product slates such as reduced gasoline production and increased diesel production. The energy and GHG emission intensity differences among these HOF options from petroleum refinery LP modeling, together with upstream production of different crude types and ethanol, are incorporated into the GREET model for WTW simulations of energy and GHG effects.

The WTW GHG emissions impacts of HOF relative to current gasoline requires accounting for vehicle efficiency gains with HOF, refinery operation changes to produce HOF, and the GHG emissions changes from blending corn and cellulosic ethanol into HOF. Detailed refinery LP simulations supplied the WTW analysis with changes in energy intensities and GHG emissions of various gasoline streams for a range of HOF market shares (3 to 71% of the total gasoline market in 2020–2030) and ethanol blending levels (E10, E25, and E40). The WTW analysis was conducted in two phases where two different types of refinery models were used. In the phase 1 analysis, ANL investigated three major refinery configurations (cracking, light coking, and heavy coking) in Petroleum Administration for Defense Districts (PADDs) 2 and 3. In the phase II analysis, ANL employed regionally aggregated refinery models for 6 different regions: PADDs 1, 2, 3 and 4, PADD 5 without California (CA), and CA individually (due to significant differences in CA refineries and regulations compared to others in PADD 5). Moreover, ANL examined several refinery capital expansion options for E10 HOF production cases.

Figure 8 summarizes the GHG reductions of HOF vehicles from miles per gallon of gasoline-equivalent (MPGGE) gains of 5 and 10%, ethanol blending, and changes in refinery operation with HOF production estimated in the phase II analysis. The results show that the impacts of HOF introduction on WTW GHG emissions were dominated by vehicle efficiency gains resulting from the use of HOF and the specific ethanol blending levels. The production efficiencies of gasoline blendstocks for oxygenate blending for various HOF blend levels (E10, E25, and E40) had only a small impact on WTW GHG emissions.

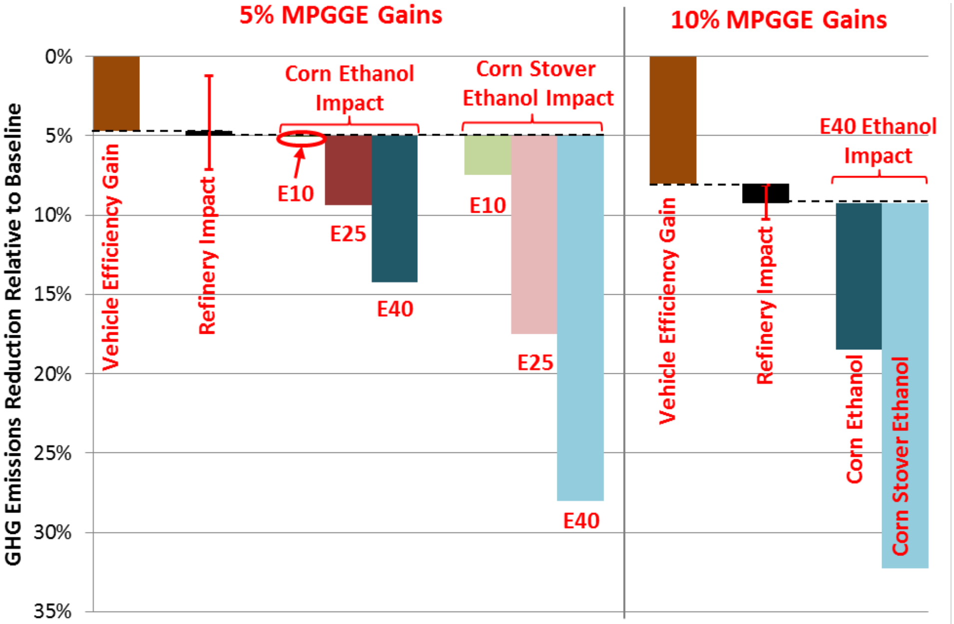

Figure 8. WTW GHG emissions reductions in vehicles fueled by HOFs with different ethanol blending levels relative to regular gasoline (E10) baseline vehicles.

These results from aggregated refinery LP models were generally consistent with those from configuration refinery LP models in the phase I study. The 5 and 10% MPGGE gains by HOF vehicles reduced the WTW GHG emissions by 4 and 8%, respectively, relative to baseline E10 gasoline vehicles. Additional 4 and 9% reductions in WTW GHG emissions can be realized with E25 and E40 blending of corn ethanol, respectively (corn ethanol GHG reductions were simulated with GREET). With corn stover ethanol blending, the additional WTW GHG reductions were 2, 12, and 23% for E10, E25 and E40, respectively. On the other hand, the changes in refinery operations needed to produce HOFs with various

HOF market shares and ethanol blending levels had a much smaller impact on changes in WTW GHG emissions (~1%). The WTW analysis shows that ethanol can be a major enabler in producing HOF and can result in additional reductions in WTW GHG emissions compared with regular E10 gasoline.

Additionally, our regional WTW analysis in Figure 9 showed that the WTW GHG emission reductions by HOF vehicles fueled by E25 HOF relative to E10 baseline vehicles are fairly consistent at 8–9% (or 36–40 g CO_2e/mile driven) throughout all regions when corn ethanol is used for ethanol blendstock. The reduction in the WTW GHG emissions is driven largely by the low GHG emissions associated with ethanol blendstock and the (assumed) 5% vehicle efficiency gain. The key driver for the regional differences in the WTW GHG emissions is the crude quality, in addition to refinery operation. For example, the WTW GHG emissions of PADDs 2 and 4, in which a large amount of Canadian oil sands are consumed, were much greater compared to other regions.

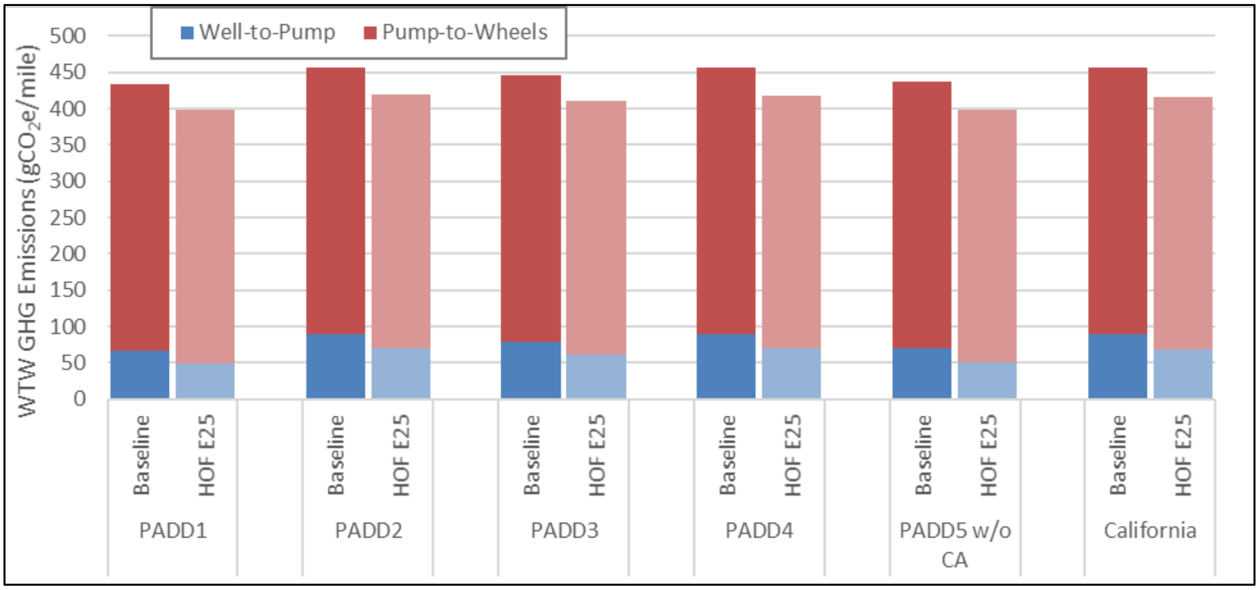

Figure 9. WTW GHG emissions (g CO_2e/mile driven) by HOF vehicles fueled with E25 HOF as compared with regular gasoline vehicles in the non-HOF baseline scenario by region.

As the ethanol blending levels are assumed to increase beyond 25%, more gasoline blendstocks shift from high octane, mid-level ethanol gasoline to gasoline available for export. It is interesting that the efficiency of refining the total gasoline blendstocks (domestic regular and HOF gasoline plus export gasoline) was also unchanged with different ethanol blending levels and market shares. However, many changes in gasoline components (e.g., reformate, alkylate, naphtha) were observed in the domestic gasoline blendstock and export gasoline pools. This is likely a result of simply moving HOF gasoline components displaced by ethanol into the export pool.

MARKET ANALYSIS

Analysis was performed assessing the economic and regulatory barriers to the introduction of a 25% and a 40% ethanol HOF into the market, including options for overcoming these barriers. This included investigation of attractions and deterrents for HOF introduction for key stakeholder (market) groups and assessment of market potential. The four stakeholder groups included fuel producers/ distributors, fuel retailers, vehicle manufacturers, and consumers. Assessments included the market effects and benefits of

HOF with regard to increasing ethanol use; achieving the RFS2 (or variant) in a timely, cost-effective way; reducing fuel costs, and providing consumer and economy-wide benefits. Results included ways of enhancing the HOF business case that circumvent difficulties faced by E85 and E15 (Johnson et al., 2015).

The participation of four main stakeholder groups was predicated upon the benefits of HOF outweighing the costs. Drivers using HOF have the potential to benefit from projected fuel cost savings, reduced price volatility, increased torque in performance applications, and the energy security and environmental attributes. Vehicle manufacturers could benefit from HOF as a means to meet future fuel economy and GHG requirements and as a way to increase torque in performance applications. Fuel retailers could obtain higher per-gallon profit margins from HOF than from gasoline, could see increased visits to their stores as a result of the potentially lower price of HOF versus gasoline, and could use HOF as a means to differentiate their stations from the competition. Fuel producers have the potential to benefit from HOF as a way to comply with RFS2, because the boost in ethanol demand could come at a strategic time for the transition to cellulosic ethanol, and because it could enable the use of less expensive fuel blendstocks.

Despite the potential benefits of HOF, there are also barriers and associated costs that must be resolved before it is adopted at large scale. Thirty of these barriers were identified through interviews with 16 companies and industry associations representing fleet managers, individual drivers, vehicle manufacturers, vehicle dealers, retail fuel stations, ethanol producers (corn and cellulosic), large oil companies, and midstream fuel distributors. This barrier identification was supplemented by information from literature reviews and HOF-related workshops. Ninety-four potential strategies to curtail these barriers were also identified and explored. Complementary subsets of these strategies were grouped into eight deployment scenarios.

The eight deployment scenarios were modeled by the Automotive Deployment Options Projection Tool (ADOPT) to estimate the adoption rate of HOF vehicles. All scenarios showed the potential for HOF vehicles to comprise a substantial percentage (43−79%) of the light-duty vehicle stock by 2035. In general, more HOF vehicles were adopted if HOF was E40, because they offer greater fuel cost savings and offer vehicle manufacturers a greater GHG emissions benefit than if the HOF were E25. The estimated HOF vehicle penetration from ADOPT was then used as an input to analyze potential impacts of HOF on the fuel supply chain. The Biomass Scenario Model (BSM) and the BioTrans model were used for this scenario analysis. The two models are complementary because they focus on different ways that HOF-related investments could be made along the fuel supply chain.

The modeling analyses concur that feedstock availability and cost are not expected to be obstacles to the substantial development of a HOF market, across all of the scenarios considered. In numerous scenarios, HOF costs were sufficiently competitive that a substantial market share was attained—up to 75 billion gallons of E40 or 30 billion gallons of fuel ethanol by 2035. This would meet over 60% of light-duty vehicle fuel demand in that year, according to projections from the ADOPT model. However, all scenarios fell short of 100% of the fuel demand of light-duty vehicles and were therefore limited. The limiting factors affected the eight scenarios in the following pattern:

1. Recognizing that regulations not taking HOF into account would be a limiting factor, most scenarios included the following assumptions:

    a. HOF is registered as a fuel and listed as a certification fuel.

    b. RFS2 is set to increase predictably, so that renewable identification number prices remain within historic levels.

    c. Future fuel economy and GHG regulations are set so their accounting systems adequately reward the production of HOF vehicles.

2. Fuel retailers' investment in HOF-compatible equipment was a limiting factor in many scenarios. At varying degrees of market penetration, the economics were marginal for certain retailers to invest. Retailer decisions to invest in HOF equipment were no longer the limiting factor if the following elements were in place:

    a. The retailer is incentivized to invest through a grant, rebate, or tax credit. Scenarios in which incentives covered 40% of investment had greater market penetration, which increased even more when 80% of costs were covered.

    b. Retail equipment cost is reduced by incentivizing equipment manufacturers, by assisting in development of equipment, by subsidizing the equipment, or through economies of scale. These strategies assume a competitive market in which savings to equipment manufacturers result in lower equipment price.

    c. Only HOF-compatible equipment is sold in advance of HOF introduction, which would effectively reduce the up-front cost for retailers that had retired and replaced their equipment after normal useful life.

3. The number of new biorefineries that can be constructed in a year was the limiting factor in scenarios that were not limited by the retail investment barrier, especially in the early years of rapid-growth scenarios. This constraint resulted in a higher ethanol price, which could subsequently deter the use of HOF. This barrier was adequately curtailed in scenarios where:

    a. Enough time passed to allow biorefinery construction to catch up with ethanol demand. This happens around 2025 in applicable cases.

    b. Biorefinery construction was performed at an annual rate greater than previously seen in the United States.

4. HOF vehicle adoption was the limiting factor for the two scenarios in which adequate retailer investment had been made and biorefinery construction had caught up with demand. The specific level of HOF vehicle adoption depended on a number of factors:

    a. More HOF vehicles are adopted if HOF is E40 because it offers greater fuel cost savings to drivers and greater fuel economy/GHG emissions benefits to vehicle manufacturers under future regulations that sufficiently reward the fuel economy benefits associated with HOF.

    b. Proactive vehicle conversion schedules, in which entire model lines are converted to HOF vehicles, result in greater estimated HOF vehicle adoption than conversion schedules that follow market demand.

    c. ADOPT estimated that a $2,500 incentive to the driver would significantly increase HOF vehicle adoption.

The need for feedback loops between the vehicle model and the fuel models was identified during this analysis. Such feedback loops were established between the ADOPT and BSM models, a baseline scenario was run, and sensitivity analyses were performed on variables deemed influential. These runs provided new insight into the interrelationships between the vehicle and fuel supply industries under various deployment, incentive, and external conditions. These insights were reported in Newes et al. 2015. The combined vehicle and fuel supply model is also available to use in future market analyses.

HIGH OCTANE FUEL INFRASTRUCTURE

RETAIL STATIONS

A major objective was to identify the issues associated with storing and dispensing a new fuel in the existing infrastructure, considering both the aboveground and the underground equipment. A service station consists of many interconnected pieces of refueling equipment necessary to deliver fuel to vehicles. There are approximately 60 pieces of equipment at a station designed to handle fuel and vapor and regulations require nearly all of this equipment to be compatible with the fuel stored. Two questions considered in introducing a new fuel to existing infrastructure are:

- Is the infrastructure compatible?
- Is the equipment listed by a third party or approved by the manufacturer for use with a specific fuel?

A significant amount of research and regulatory action has addressed these concerns with positive progress toward enabling the use of ethanol blends higher than E10 in existing and upgraded equipment. The issues for deploying equipment handling higher ethanol blends center on cost considerations and station knowledge of fueling equipment - rather than technical issues. A potential barrier is that stations are not required to keep records of equipment if they are selling E10 or lower ethanol gasoline. This makes it difficult to determine if existing equipment is compatible with various ethanol blends. For aboveground equipment, UL-listed E25 and E85 equipment (which satisfies federal and local regulations) is available. The price premium for E25 equipment is minimal compared to conventional E10 equipment, whereas the price premium is significant for E85 due to the use of specialized metals (Johnson et al., 2015; Moriarty, Kass and Theiss, 2014). Interested parties have suggested testing E25 equipment to see if it can be recertified by UL for E30 or E40. Credit card companies are switching to chip and pin cards, which will result in many dispensers being upgraded or replaced to accommodate the new cards by October 2017. This is a large, near-term opportunity to upgrade dispensers to accommodate higher-level ethanol blends.

EPA's Office of Underground Storage Tanks regulates underground storage tanks (USTs) per Code of Federal Regulation (CFR) Title 40 Subtitle 1 Subchapter 1 Parts 280-282. The federal UST regulation was updated in October 2015 with section CFR 280.32 in the 2015 UST regulation providing clarity to the 1988 compatibility requirement by specifying additional compatibility requirements for owners and operators wishing to store certain regulated substances, including fuels containing more than 20 percent biodiesel (and 10 percent ethanol). All portions of an UST system must be compatible with the fuel stored. Demonstrations of compatibility must be provided for the: tank, piping, containment sumps, pumping equipment, release detection equipment, spill equipment, and overfill equipment. The requirements are:

1. Owners of USTs switching to store blends containing greater than 20% biodiesel or 10% ethanol must notify their implementing agency (usually a state office) 30 days prior to switching fuels to store an E10+ (or B20+) blend.

2. Owners of USTs storing greater than E10 must demonstrate compatibility through either:

    a. Certification/listing of equipment for use with the fuel stored by a nationally recognized, independent testing laboratory or

   b. Equipment or component manufacturer approval for use with the fuel stored. This written statement must affirm compatibility and list the specific ranges of biofuel blend the equipment or component is compatible with or
   c. Use of another option determined by the implementing agency to be no less protective of human health and the environment.

3. Owners of USTs storing fuels containing greater than 10% ethanol must maintain records demonstrating compatibility as long as the fuel is stored.

TERMINALS

Terminals are an important part of the transportation fuel supply chain moving products to end-user markets. Their primary function is to store and distribute fuels. The Oil Price Information Service reports that there are 1,296 terminals storing transportation fuel nationwide, and nearly all either store ethanol or are capable of storing it (OPIS, 2015). Terminals store all fuel components separately (i.e., gasoline blendstock, ethanol, additives), and they are blended in-line as they are delivered to transport trucks. Many companies with terminals are also obligated parties under RFS2, and they may see a benefit in deploying more ethanol capacity to meet their volume requirements and see it as a potential revenue stream through renewable identification number markets.

While there are no technical barriers to storing more ethanol, there are several non-technical factors that could limit increased deployment of ethanol at terminals, including: terminal companies report that nearly all tanks are in-use, and there is a lengthy permit process to build a new tank if needed; land to add new tanks and off-loading facilities may not be available; increased truck traffic to deliver ethanol could be problematic for some terminals; pipeline companies own many terminals and lease tanks to customers under long-term contracts for storage of specific fuels, thus there would have to be a strong business case to motivate terminals to add off-loading, and loading bay equipment and additional tanks if no existing ones are available. Many terminals receive ethanol from rail trans-modal facilities and further study is required to determine the ability of trans-modal facilities to handle more ethanol.

LOW-COST POTENTIAL HOF BLENDSTOCKS

The important objective of quantifying the potential of low cost HOF formulated with natural gasoline was addressed by the following activities:

- Examine the ranges of composition and properties for natural gasoline sold in the US market.

- Determine the properties of blends of various natural gasolines and ethanol at different blend levels.

- Develop a model to predict natural gasoline–ethanol blend vapor pressure for Flex Fuel (ASTM D5798 compliant fuel).

Samples of natural gasoline were obtained from eight sources covering the range available in the market. These were assessed for chemical composition using detailed hydrocarbon analysis (ASTM D6730: high-resolution gas chromatography to identify individual components of gasoline) and by benzene analysis (ASTM D3606). Sulfur, Reid vapor pressure (RVP), and RON were determined by appropriate ASTM methods.

A subset of samples meeting the current benzene limit and the proposed Tier 3 sulfur limit, and covering the range of composition and properties, were blended to produce E30 (HOF) and Flex Fuel (E51, E70, and E83). The vapor pressure, RON, and MON were measured. For the E30 blends, NREL also measured the distillation curve (ASTM D86) and vapor lock protection class (Alleman, 2015).

NREL has used a modeling approach based on the Wilson equation and on considering the gasoline as a pseudo-component to successfully predict the vapor pressure of gasoline–alcohol blends to within 0.7 kPa (Christensen, 2011), which is more precise than the repeatability of the vapor pressure measurement method (2 kPa for ASTM D5191). This modified Wilson method was applied to the blends to determine its suitability for predicting RVP to eliminate the need for RVP testing of the final blend, thus eliminating the need for additional testing at the terminal. The modeling approach showed that the RVP for the finished fuel could successfully be estimated from the RVP of the blend components for this work. These results have been published in a peer-reviewed journal (Alleman, 2015).

Key outcomes from this research (Alleman, 2015) include:

- Natural gasoline samples in this project consisted of 80–95% paraffinics, 5–15% naphthenics, 3% or less aromatics, and the balance olefins. Paraffins were typically n-pentane and iso-pentanes.

- Benzene content ranged from approximately 0.1 to 1.2 wt %, so blends of E30 and E40 would meet EPA limits for benzene content in gasoline.

- Sulfur content ranged between 4 and 145 ppm. Assuming an ethanol content of 51 vol % (Flex Fuel minimum ethanol content), a natural gasoline blendstock would be required to have 20 ppm sulfur or less for the finished fuel to meet the EPA Tier 3 gasoline sulfur limit.

- Vapor pressure (ASTM D5191-13) ranged from 12.9 to 14.6 psi. Because of the high vapor pressure, over 70 vol % ethanol could be blended into Flex Fuel while still meeting the class 4 (wintertime) minimum vapor pressure requirement of 9.5 psi. For blending of class 1 (summertime) Flex Fuel, a minimum of 74 vol % ethanol was required to stay below the 9 psi upper limit on vapor pressure.

- Modeling of vapor pressure using universal quasichemical functional-group activity coefficients (UNIFAC) and Wilson equation-based approaches provided good agreement with experimental data for most samples.

- The RON for the natural gasoline ranged from 67 to 72. When it is blended with ethanol, the 91 RON level typical of finished regular gasoline would be met with approximately 30 vol % ethanol. Natural gasoline is a volatile, low-cost blendstock for Flex Fuel. For a high-octane mid-level blend, natural gasoline could only be used as a blending component.

CONCLUSIONS

The experimental and analytical results of this study considered together show that HOF, specifically mid-level ethanol blends (E25-E40), could offer significant benefits for the United States. These benefits include an improvement in vehicle fuel efficiency in vehicles designed and dedicated to use the increased octane. The improved efficiency of 5-10% could offset the lower energy density of the increased ethanol content, resulting in volumetric fuel economy parity of E25-E40 blends with E10. Most of the flex-fuel vehicles on the road today would be expected to have faster acceleration using HOF, which offers a marketing opportunity in the near term. Furthermore, dedicated HOF vehicles would provide lower well-to-wheel GHG emissions from a combination of improved vehicle efficiency and increased use of ethanol. If ethanol were produced using cellulosic sources, GHG emissions would be expected to be up to 30% lower than those from E10 using conventional ethanol and gasoline. Refinery modeling suggests that refiners could use higher levels of ethanol to meet potentially high market shares of HOF.

Analysis of the HOF market and the primary stakeholders reveals that the automotive OEMs, consumers, fuel retailers, and ethanol producers all stand to benefit to varying degrees as HOF increases its market share. The results depend on the underlying assumptions; but HOF offers an opportunity for improved fuel economy, and these dedicated vehicles are likely to be appealing to consumers. The possible limiting constraints to significant HOF market penetration were identified. Regulatory uncertainty and insufficient retailing investment were considered the most likely constraints to limit the introduction of HOF. HOF could be limited by the rate of construction of additional integrated biorefinery capacity, and poor dedicated HOF vehicle penetration would also limit the overall HOF market. Feedstock availability was not found to limit the growth of HOF.

It would be a significant benefit if a new fuel utilized the existing infrastructure. Our findings were that neither technical nor materials obstacles are likely to prohibit HOF, but new aboveground equipment compatible with HOF will need to be installed. Sufficient capacity was found to allow the introduction of HOF at the nation's terminals.

Overall blendstock costs are not a significant barrier to HOF introduction and the low cost of natural gasoline makes it attractive to consider for a blending component. The properties of HOF, when using natural gasoline as the sole blendstock, can be predicted with sufficient accuracy using industry-accepted models for RVP. The use of these models to predict final RVP of the finished blend eliminates the need for additional test capability at terminals and reduces a barrier to introduction of this type of HOF blend.

REFERENCES

Alleman, T. L., R. L. McCormick, and J. Yanowitz, "Properties of Ethanol Fuel Blends Made with Natural Gasoline," *Energy Fuels* **29** 5095-5102 (2015).

Anderson, J. E., et al., "High Octane Number Ethanol-Gasoline Blends: Quantifying the Potential Benefits in the United States," *Fuel* **97**, 585–594 (2012).

Car and Driver, "Drivelines: Chevrolet Silverado V6," *Car and Driver* **59**(9), March 2014, pp. 102–13 Available at http://www.caranddriver.com/reviews/2014-chevrolet-silverado-v-6-instrumented-test-review. Accessed July 2016.

Christensen, E., et al., "Renewable Oxygenate Blending Effects on Gasoline Properties," *Energy Fuels* **25**(10) 4723–4733 (2011).

Chupka, G.M., et al., "Heat of Vaporization Measurements for Ethanol Blends Up To 50 Volume Percent in Several Hydrocarbon Blendstocks and Implications for Knock in SI Engines" *SAE Int. J. Fuels Lubr.* 2015, doi:10.4271/2015-01-0763.

Hirshfeld, D. S., et al., "Refining Economics of U.S. Gasoline: Octane Ratings and Ethanol Content," *Environ. Sci. Technol.* **48**, 11064–11071 (2014). doi:10.1021/es5021668

Johnson, C., Newes, E., Brooker, A., McCormick, R., Peterson, S., Leiby, P., Martinez, R.U., Oladosu, G. and Brown, M.L. (2015). High-Octane Mid-Level Ethanol Blend Market Assessment. NREL/TP-5400-63698.

Jung, H., et al., "Fuel Economy and CO_2 Emissions of Ethanol-Gasoline Blends in a Turbocharged DI Engine," *SAE Int. J. Engines* **6**(1) (2013). doi:10.4271/2013-01-1321

Leone, T., et al., "Effects of Fuel Octane Rating and Ethanol Content on Knock, Fuel Economy, and CO_2 for a Turbocharged DI Engine," *SAE Int. J. Fuels Lubr*. **7**(1), 9–28 (2014). doi:10.4271/2014-01-1228.

Moriarty, K., M. Kass, and T. Theiss, "Increasing Biofuel Deployment and Utilization through Development of Renewable Super Premium: Infrastructure Assessment," NREL/TP-5400-61684, November 2014.

Newes, E., Johnson, C., Brooker, A., Peterson, S. (2015). Draft Integrated Market Analysis of High-Octane Mid-Level Ethanol Blends.

Oil Price Information Service (OPIS). 2015. Petroleum Terminal Encyclopedia. Available for purchase at: http://www.opisnet.com/products/liquid-terminals-directory.aspx

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):80-90, 2016, doi:10.4271/2016-01-0836.

Splitter, D. A., and J. P. Szybist, "Experimental Investigation of Spark-Ignited Combustion with High-Octane Biofuels and EGR. 2. Fuel and EGR Effects on Knock-Limited Load and Speed," *Energy & Fuels* **28**(2), 1432–1445 (2014). doi:10.1021/ef401575e

Splitter, D. and J. Szybist, "Intermediate Alcohol-Gasoline Blends, Fuels for Enabling Increased Engine Efficiency and Powertrain Possibilities," *SAE Int. J. Fuels Lubr.* **7**(1) (2014). doi:10.4271/2014-01-1231

Szybist, J., et al., "Investigation of Knock Limited Compression Ratio of Ethanol Gasoline Blends," SAE Technical Paper 2010-01-0619, 2010, doi:10.4271/2010-01-0619.

Szybist, J. and B. West, "The Impact of Low Octane Hydrocarbon Blending Streams on the Knock Limit of "E85," *SAE Int. J. Fuels Lubr.* **6**(1),44–54 (2013). doi:10.4271/2013-01-0888

Thomas, J. F., B. H. West, and S. P. Huff, *Effects of High-Octane Ethanol Blends on Four Legacy Flex-Fuel Vehicles, and a Turbocharged GDI Vehicle*, ORNL/TM-2015/116, March 2015. Available at http://info.ornl.gov/sites/publications/files/Pub54888.pdf