Fuel Additives for Future Fuel and Vehicle Technologies

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1. INTRODUCTION

We are currently in the midst of a rapid evolution in the transportation sector. Over the next 10 to 20 years, the efforts to improve efficiency, fuel economy and reduce emissions will be the dominant factors driving change in engine and fuel technology. Over time, the most effective means of meeting the efficiency and emission goals will become clear, however, the direction for change is apparent and some of the first steps required for engines and fuel technology are well known. A key factor that is enabling the evolution in both the engine and the fuel is the development of effective fuel additive technology that allows for the production and safe distribution of quality transportation fuel and ensures optimal engine performance.

This paper will review the general classes of additives used to ensure production of high quality fuel and explore performance attributes of fuel additives that are enabling vehicles and fuels to evolve to meet tighter fuel economy and emission requirements.

2. THE ROLE OF FUEL ADDITIVES IN PRODUCING QUALITY TRANSPORTATION FUEL

The properties and sources of transportation fuel are rapidly evolving, driven by regulation, energy policy and consumer pressures. The changes are motivated by sometimes conflicting desires to support local economies, improve efficiency, improve energy security, and reduce emissions or lower fuel carbon footprint. These different drivers lead to major changes in gasoline and diesel fuel quality and production source. Table 1 and 2, provide a summary of the major changes to gasoline and diesel fuel that will potentially require a fresh look at additive technology and their applications as these fuel changes evolve. The Tables also provide a brief summary of the primary drivers for the fuel change. This paper will focus on transportation fuel sulfur reduction and rapidly increasing use of renewable fuels.

Fuel sulfur reduction is directly related to reducing sulfur based emissions such as sulfated particulates and sulfur dioxide and enabling engine and after treatment technology. Desulfurization can lead to reduced gasoline octane pool. The introduction of ultra low sulfur diesel fuel has generally resulted in reduced fuel lubricity, conductivity and low temperature properties while enhancing cetane quality and stability.

The use of renewable fuels are encouraged as their use in both gasoline and diesel fuel can reduce dependence on crude oil and often, directly reducing emissions including greenhouse gas emissions. The use of renewable fuels is not new. Ethanol derived from grain has been used for many years in the U.S., mainly to support the agricultural industry, and by Brazil to displace crude oil. Concern about the real environmental benefit of ethanol made from grain has lead to focus on non-crop based ethanol and increased research into less carbon intensive methods of producing renewable

ethanol such as cellulosic ethanol. Blending ethanol into gasoline increases the octane pool but can bring with it a number of storage, transportation and vehicle compatibility issues (Table 1)

Diesel fuel derived from renewable biomass has been used as means to reduce use of petroleum feed stocks and support local economies. The primary renewable diesel fuel today consists of fatty acid methyl esters (FAME) produced from vegetable oil or animal fat. FAME can be used by itself to power a diesel engine but is more often blended with petroleum based diesel fuel in at levels of 2% (B2), 5% (B5), 10% (B10) or higher. More recently, the focus of renewable fuels has shifted to reducing the carbon foot print from the transportation sector. The addition of FAME to a petroleum based diesel may bring improved fuel lubricity, but harm cold temperature properties or fuel stability (Table 2).

Renewable oils, such as vegetable oils and rendered animal fats can also be brought directly into the refinery to produce “renewable” diesel. The oils and fats can be blended directly with other feed streams prior to diesel hydroprocessing or processed directly in units designed to convert oils and fats directly into high quality diesel blend components. The processed renewable oils are highly paraffinic materials and can be directly blended into the petroleum based diesel. These products are very low in sulfur and have high cetane quality, but poor low temperature and lubricity properties.

The production of transportation fuel through gas to liquids technology is attracting a significant level of attention. Whether the source of synthesis gas in this process comes from biomass (BTL), coal (CTL) or natural gas, the approach provides a potential means to reduce dependency on petroleum sources for liquid fuels. In the case of BTL, the approach can significantly reduce well to wheels carbon emissions. A fuel containing substantial portion of liquids derived from syngas is expect to have some unique properties. For example, BTL diesel would be expected to display higher cetane but suffer from lubricity and cold flow issues compared to petroleum based fuel.

Fuel additives are being developed and employed to address the specific needs that are arising as sulfur is removed from fuels and renewable fuels and blend stocks are more widely used. One category of additives function to ensure a fuel possesses appropriate properties required for the manufacture, distribution and storage of the fuel. A second category of additives is designed to influence cleanliness and combustion characteristics of the fuel to ensure that fuels with widely varying composition provide needed performance in an engine. The next two sections address the potential need for these two categories of additives.

2.1. Fuel Additives Used to Maintain Fuel Integrity and Distribution Safety and Efficiency

2.1.1. Antioxidants and Stabilizers

With the progression of time, fuel degradation is not uncommon. Degraded fuels can form gums and sediment that plug fuel filters, create deposits on sensitive fuel system components and interfere with the proper operation of motor vehicles. Due to these common features, fuel specifications often include performance tests, such as oxidative and thermal stability tests, to ensure the fuels are fit for use in the marketplace. The type of degradation that occurs, however, is different for gasoline and diesel fuels.

Gasoline can undergo oxidative degradation and form gum deposits in engine components that lead to poor drivability and increased emissions. Fuels with high olefin and diene concentrations are

typically more susceptible to oxidation. To control gum formation in gasoline, refineries use phenolic and aromatic amine antioxidants. Antioxidants are most effective when they are added to reactive blend streams such as cat cracked (FCC), coker or polymeric gasoline streams as they are produced. Once the degradation process begins it becomes more difficult to control. One of the benefits of desulfurization of gasoline is the improvement in its oxidative stability. Many of the reactive species in gasoline are removed during desulfurization and normally only low concentrations of antioxidants are needed to control oxidation in low sulfur gasoline. Gasoline blended with ethanol has similar stability properties as the hydrocarbon base gasoline.

Unlike gasoline, diesel fuel normally degrades by mechanisms other than oxidation. Frequently, heterocyclic and other sulfur and nitrogen containing molecules that result from cracking heavier streams to make diesel and gasoline blend components will react with each other or acidic components found in other diesel fuel blend components. These types of reactions result in the formation of sediments, which can plug fuel filters and deposit in critical fueling locations, such as fuel injectors that can result in power loss, smoke and higher overall emissions. Amine-based additives, sometimes combined with dispersants, are used to control the stability of diesel fuel. Deep desulfurization or hydro-processing (normally used to make ultra-low sulfur diesel fuel) will eliminate most of the reactive species found in higher sulfur diesel fuel. Ultimately, hydroprocessing produces a very stable diesel fuel requiring the use of little, if any, stability additive. Biodiesel, while normally low in sulfur, degrades through an oxidative process that is controlled using hindered phenol antioxidants. It is important to treat biodiesel when it is produced.

Both gasoline and diesel fuel are occasionally contaminated with metals, such as copper, that can catalyze the formation of gums and sediment. Consequently, metal deactivators are used to neutralize the catalytic effect of these metals. Most biodiesel antioxidants contain a metal deactivator to control catalytic degradation.

Table 3 provides a summary of antioxidant and stabilizer chemistries used in fuels and their primary applications.

2.1.2. Cold Flow Improving Additives

Diesel fuel contains naturally occurring paraffinic molecules distilled from crude oil. The source, chemical composition and processing of the crude oil determines the concentration and distribution of these saturated, straight-chained molecules in the fuel. Higher molecular weight paraffins have limited solubility in diesel fuel and precipitate from the bulk fuel in the form of wax crystals when the fuel cools. This separation occurs at the cloud point, the temperature where wax crystals precipitating from diesel fuel become visible to the naked eye. As more wax precipitates, large plate-like crystals begin to develop. These crystals can restrict the flow of diesel fuel from storage tanks and pipes and plug vehicle fuel filters, resulting in an engine's loss of power or inability to start. In the winter, kerosene or No. 1 diesel fuel, if available, can be added to No 2 diesel fuel to dilute the higher MW paraffin concentration and lower the cloud point of the fuel. If kerosene is not available or is not economical to use as a diluent, cold flow improving (CFI) or wax crystal modifying additives can be used to improve the low temperature properties of diesel fuel. Frequently, a combination of kerosene and CFI is used to improve diesel fuel low temperature properties.

CFIs can be divided into two different categories: I. Pour point depressants, and 2. Operability additives.

Pour point depressants are used to keep diesel fuel fluid and transportable. They co-crystallize with paraffins coming out of solution as a fuel cools and disrupt the structure of the wax crystals. Pour point depressants can also reduce the size of wax crystals, but not necessarily to a size where they will pass through a vehicle fuel filter. Fuels are normally treated with pour point depressant at the refinery.

Operability additives are designed to improve the filterability of diesel fuel through diesel fuel filters at low temperatures. Effective operability additives function as wax crystal nucleators, crystal modifiers and crystal dispersants. When a fuel cools, nucleators precipitate from the fuel as wax crystals begin to precipitate and offer many sites for the initiation of wax crystal formation. With many nucleating sites, the crystals remain small and are able to pass through vehicle fuel filters without plugging them. Operability additives normally treat at considerably higher treat rates compared to pour point depressants.

Biodiesel in general has a negative effect on the low temperature properties of diesel fuel and an additive's ability to improve the low temperature properties of biodiesel blends. This is also true with renewable fuels derived from refineries processing oils and fats in hydroprocessing units or with Fischer Tropsch diesel fuel derived from biomass to liquids processes. Renewable diesel fuel and blend components have a high paraffin content. In all cases, greater concentrations of less soluble paraffin and biodiesel components precipitate when a fuel cools and are more difficult to control. Figure 1 illustrates the impact of treat rate of CFI additives on the cold filter plugging point of base diesel fuels and the base fuel containing soy methyl ester (SME) biodiesel.

When fuel below its cloud point remains undisturbed for a period of time, wax crystals tend to settle to the bottom of the vessel containing the fuel, causing stratification of the wax in the fuel. This results in different cloud points between the top and bottom of the fuel in its storage or fuel tank. To control wax settling to the bottom of a diesel fuel tank, wax anti-settling additives (WASA) are used to disperse the wax throughout the fuel tank. Table 4 shows the impact of wax settling on the cloud point of fuel with and without additives providing WASA performance.

Typically, ethylene vinyl acetates (EVA), copolymers and terpolymers and their derivatives form the core of a today's cold flow packages. Other proprietary components enhance the performance on these polymers.

2.1.3. Lubricity

The diesel fuel fraction of crude oil contains sulfur and nitrogen compounds that provide natural lubrication to protect vehicle fuel pumps and injectors from wear. With mandated desulfurization of diesel fuel in many parts of the world, these naturally occurring lubricity components are being removed from diesel fuel, resulting in fuel that increases wear and eventual failure of critical vehicle fuel-delivery components.

Low sulfur (LSD) and ultra low sulfur (ULSD) diesel fuels are frequently additized with lubricity additives to protect critical injection system components. Lubricity additives are generally classified

as neutral or acidic. Neutral additives, esters and amides, normally require higher treat rates compared to more cost-effective, mono-acid lubricity additives (Figure 2).

Biodiesel fuel has chemistry similar to some lubricity additives and when blended with diesel fuel provides significant improvement to the fuel's lubricating properties and in many cases eliminating the need for additional lubricity additives. (Figure 3) Renewable diesel does not provide lubricity benefits when incorporated into traditional diesel fuel and therefore, must be treated with lubricity additives.

2.1.4. Pipeline Corrosion Inhibitors

Most diesel fuel and gasoline at some point are transported through a mild carbon steel pipeline and stored in mild carbon steel storage tanks. Fuel commonly contains small quantities of dissolved water that can become free water when the fuel cools. Free water can cause internal corrosion in pipelines and storage tanks, thereby producing fine rust that coats the inside of pipeline and storage tank walls. This rust can increase drag in the pipeline resulting in decreased pumping efficiency and higher energy costs. Fine rust particles can also separate from the pipeline and storage tank walls and create unnecessary wear on critical pipeline metering and pumping equipment, resulting in high-maintenance costs and frequent cleaning. Rust inhibitors, such as dimer, trimer and alkyl succinic acids, are normally used to protect the distribution system from corrosion. By forming a thin film on the pipeline wall, the rust inhibitors protect the distribution system from oxidative corrosion caused by water and oxygen.

Biodiesel blends and gasoline containing ethanol can have corrosion issues if the renewable fuels are not free of contaminates which can come from the manufacture of the fuel or in the handling and distribution of the fuel. For instance, metal salts found in some biodiesels can increase the corrosively of the fuel. Typical pipeline corrosion inhibitors can provide protection for biodiesel fuels.

Unlike biodiesel, traditional additives used to protect pipelines are not optimal for gasoline containing ethanol. Since ethanol and water can phase separate from gasoline when exposed to moderate levels on water, ethanol corrosion inhibitors should be designed to not only protect from corrosion in the hydrocarbon phase but also the ethanol water phase if phase separation should occur. Some ethanol corrosion inhibitors provide buffering properties designed to control the pH of the ethanol. Caution should be taken in selecting ethanol corrosion inhibitors as some can increase engine intake system deposits, especially in high ethanol content fuels such as E-85.

2.1.5. Other Corrosion Inhibitors

Although iron oxidation is a major cause of fuel system corrosion, other non-ferrous components are also susceptible to corrosion caused by reactive sulfur species found in some diesel fuels and gasoline. As a result, many fuel specifications have copper corrosion limits as determined by a copper strip test. Typically thiadiazole chemistry is effective at controlling copper corrosion.

More recently, there have been cases of silver contacts in fuel sending/sensing units suffering damaged from free sulfur and other sulfur species remaining in gasoline after the desulfurization process. This problem has occurred sporadically in North America and the standards board, ASTM, now requires gasoline to pass a silver corrosion test in order to meet their specifications. Figure 4

illustrates the effect of free sulfur on silver strip ratings. The protection provided by two different fuel additives is shown in Figure 5.

2.1.6. Conductivity Improvers

In order to eliminate the potential for a spark to ignite fuel vapors, for years jet fuel, and in some cases, other distillate fuels, have been treated with additives to dissipate static-charge buildup. Static-charge buildup is fairly common when diesel fuel is discharged into an improperly grounded vessel such as a fuel tanker. As a result, if the tanker switches back-and-forth between hauling diesel fuel and gasoline, the potential for gasoline vapors to remain in the container while loading diesel fuel creates the risk of an explosion and fire. Desulfurization of diesel fuel significantly lowers diesel fuel's natural conductivity resulting in a greater risk of explosion or fire. To reduce the potential for static-charge buildup during transfer of fuel from one vessel to another, conductivity additives are now frequently added to ultra low sulfur diesel fuel. Fuel conductivity is temperature dependent with conductivity decreasing as a fuel cools (Figure 6). Conductivity improvers can be added at either the refinery or at terminals before the fuel is loaded into a tanker.

One benefit of biodiesel is its ability to increase the conductivity of diesel fuel. Figure 7 shows that difference sources of biodiesel have different effects on conductivity, even when they are made from the same feed stock.

2.2. Fuel Additives Employed to Modify Combustion

The combustion characteristics of fuel are generally controlled by the fuel's chemical composition. One of the key combustion properties is the ability to ignite the fuel and air charge at an optimum time in an engine. Fuel ignition is a radical-driven reaction, and properly designed fuel additives can have a significant impact on ignition, enhancing or retarding the propensity for ignition.

2.2.1. Diesel Ignition Improving Additives

The cetane number of diesel fuel is a measure of the fuel's propensity to ignite and directly impacts an engine's ability to start and efficiently burn fuel. Unlike gasoline engines that initiate combustion using a spark plug, diesel engines ignite fuel by compressing the atomized fuel in the combustion chamber. Once under pressure, the fuel heats and undergoes spontaneous ignition. The chemical composition of diesel fuel determines its cetane quality. Fuels with higher paraffin content tend to have a higher cetane quality, while more aromatic and unsaturated components have a lower cetane quality. The lower the diesel fuel's cetane number, the longer the fuel's ignition delay time will be, making the fuel's ability to ignite in the combustion chamber much more difficult. This longer ignition delay leads to incomplete combustion, loss of power and increased gaseous, particulate and white smoke (unburned fuel) emissions. Energetic cetane improving additives are added to diesel fuel to reduce the ignition delay time which results in improved startability, less noise and lower overall emissions. Figure 8 illustrates the delay in ignition observed for a base fuel versus base fuel to which a cetane improver additive was added to yield a ten cetane number increase.

A primary pollutant from the diesel engine is NOx. Numerous studies have demonstrated that increasing the cetane number of a fuel will result in general reduction in NOx emission from a diesel engine. This is a result of the shorter ignition delay time for higher cetane fuels and subsequently lower peak temperatures within the diesel engine. The US EPA conducted a thorough analysis of

cetane quality impact across a broad range of fuels and engine types. Figure 9 illustrates the typical levels of NOx reductions obtained using additives to increase cetane. Figure 10 illustrates to reductions in HC, CO and particulates from this same study. Significant reductions in NOx, CO, HC and in some cases particulate emissions are achievable using cetane improving additives.

Commonly used additives with demonstrated capability to improve fuel cetane quality include alkyl nitrates and peroxides. The alkyl nitrates are the preferred commercial source of cetane improver due to low cost and favorable handling characteristics.

Depending on the source of FAME, the use of biodiesel can increase or decrease the cetane number of a diesel fuel. This is dependent on the cetane number of the base fuel to which the biodiesel is added. In areas with low cetane number specifications such as the US, biodiesel normally increases cetane number. In regions where cetane number is high such as Europe, some biodiesels will lower cetane number. Biomass to liquids and hydroprocessed oils provide distillate blend stocks that have a very high cetane number. These make good components for blending high quality, low emissions diesel fuel.

2.2.2. Octane Improving Additives

The octane quality of gasoline measures a fuel's propensity to resist auto ignition, and is an important property for gasoline. Unlike diesel engines where compression heats the charge to ignite the fuel, gasoline engines are designed to initiate combustion through a spark from a spark plug. The chemical composition of the gasoline determines the base gasoline octane level. Molecules such as aromatics and olefins are less susceptible to spontaneous ignition under pressure and have a higher-octane value. A fuel's octane quality can be improved by the use of additives or other high-octane blend components, such as oxygenates or aromatic components that are added to fuel at levels ranging from around 1% to more than 85% in the case of E85 fuel. A very effective octane-improving additive, mmt®, methylcyclopenta-dienyl manganese tricarbonyl, improves octane number two to three RON and is used around the world at levels under 18 mg Mn/liter to increase the octane quality of gasoline.

The increased use of high octane quality blend components and the additive mmt have reduced the processing severity on gasoline blend components in refineries resulting in increased fuel volume and reduced refinery greenhouse gas emissions.

Low levels of ethanol blended with gasoline, 10% or less have little or no impact on fuel system deposits. Higher level ethanol blends such as 85%, have been shown to increase injector fouling and add to intake valve deposits. Different sources of ethanol have different deposit forming tendencies. Figure 11 illustrates these differences.

3. FUEL ADDITIVES FOR OPTIMAL VEHICLE PERFORMANCE

Throughout the world, once gasoline and diesel fuel are produced and shipped, fuel producers and marketers widely use fuel additives to improve the fuel quality and its performance in vehicles are widely. These multifunctional additive packages frequently contain dispersants or detergents designed to keep the vehicle fuel distribution systems clean and operating at optimal efficiency. These additives allow for fuel marketers to provide premium fuels to the end users and allow

performance-driven market differentiation. In some markets, government or industry require performance additives as part of a strategy to reduce emissions from motor vehicles.

Fuel efficiency is a primary force driving change in vehicle technology. Throughout the vehicle, engine and drive train, designs are evolving to improve the efficiency with which the vehicle utilizes the energy from fuel. The design changes can take the form of reduce loss in pumping efficiency and stratified charge in direct injection gasoline engines, efficient high injection pressure diesel engines or hybrid systems that recapture system energy. Table 5 captures some of the approaches currently being considered or used to improve engine efficiency. Specific components of the fuel and intake system that, due to the engine modifications, could prove susceptible to deposit formation are also listed in Table 5. In all cases, keeping the fuel and air delivery systems clean is critical to ensure optimal operation.

The following sections will consider the impact of performance of additives in a number of engine technologies designed to provide improved fuel efficiency and reduced emissions.

3.1. Diesel Performance Additives

Fuel-related deposits can form on critical diesel engine components, reducing the engine's efficiency and power, and increasing gaseous and particulate emissions. The most critical location for fuel-related deposits in modern fuel-injection systems is coking deposits located near the tip of the injector. These deposits can restrict fuel flow and modify fuel spray pattern, resulting in incomplete mixing of fuel and air, and inefficient combustion. Dispersant additives are widely used to control the formation of these types of deposits in fuel injectors.

Diesel fuel also tends to degrade when exposed to temperatures found in diesel injectors and fuel rails. Since diesel fuel in some engines is returned to the fuel tank, the heated fuel can form sediment in the tank that eventually plug fuel filters, also resulting in loss of power and performance. While dispersants can help disperse sediment, diesel stability additives are frequently added to diesel performance packages to control sediment formation.

Besides controlling deposit formation, diesel performance additives are frequently formulated with a number of other components to provide additional functionality to the package. Packages frequently contain cetane improvers, wax crystal modifiers or CFIs, combustion improvers, lubricity additives, demulsifiers, antifoaming additives and deicing additives. Since diesel fuel has a tendency to foam when fueling a vehicle, antifoams are frequently added to diesel fuel to control spillage and increase the rate of fueling diesel vehicles. The dispersant used in diesel fuel also tends to emulsify water, which can lead to plugged fuel filters. Therefore, incorporating adequate demulsifiers into the package to control water pickup by the fuel is highly important. Likewise, if water is present in a fuel, it is important to prohibit any ice crystals from forming that could also plug fuel filters. Glycol ether deicers are normally used to manage water contamination

3.1.1. High Pressure Common Rail Diesel Engine Performance

The indirect injection diesel (IDI) engine has now been replaced in the market by direct injection (DI) light duty diesel engines, for reasons of fuel economy, performance and lower emissions. For these same reasons, heavy duty engines are beginning to more widely utilize high pressure direct injection systems. The injection system deliver improved atomization and fuel air mixing but also enable the

use of multiple injections into the cylinder to more closely control the combustion event. The injectors, key components in the performance of the engine, are seen as vulnerable to having their operation perturbed by fouling from deposits, and it is viewed that this will be even more so the case for vehicles under development to meet EURO V emission regulations.

To evaluate a fuels tendency to cause injector coking or fouling, two standard test methods are widely used. The XUD9 test, CEC F-23-01, uses an older indirect injection diesel engine technology. The more recently developed CEC F-98-08 test employs the high speed direct injection Peugeot DW10 diesel engine. This engine is equipped with a common rail fuel injection system. In the DW10 test, a base fuel containing a Zn dopant is employed to promote injector coking. The relative coking level is followed by monitoring the engine power loss as the injectors foul. With the addition of an effective additive chemistry, injector deposits are prevented and no power loss is observed (Figure 12).

3.1.2. Exhaust Treatment Systems

Control and reduction of particulate matter (PM) and NOx emission from diesel engines is of increasing importance, especially in heavily congested urban areas. Advances in engine design have dramatically reduced emission of both pollutants in the most modern engines. Exhaust after treatment is also an important approach to controlling PM and NOx emissions whether the systems are used to retrofit existing vehicles or are used as part of the overall design strategy to control engine emissions.

The principle exhaust treatment approach to control PM is the diesel particulate trap (DPF). DPFs accumulate and store PM during low speed/temperature engine operation and burn the accumulated PM during high speed/temperature operation. The transition between accumulation and burning is a complex relationship between the amount of stored soot, soot accumulation rate, soot oxidation rate and temperature, exhaust flow rate, exhaust backpressure, and exhaust gas temperature and composition. Lowering the temperature at which the predominantly organic soot oxidizes with the DPF can have a positive impact on overall engine operation, leading to higher available power and fuel economy, and reduced service downtime for DPF maintenance.

There are several methods for lowering soot oxidation temperature. Most rely on use of hardware such as catalyzed traps. Another approach is to use specific diesel fuel additives that act as fuel borne catalysts. One example of a fuel borne catalyst is the fuel additive mmt, which will enhance the rate of soot oxidation. This allows the DPF to operate with less stored soot and essentially reduces the exhaust temperature required to burn out accumulated soot and regenerate the DPF. The lower exhaust temperatures required for DPA trap regeneration would enable regeneration to occur on vehicles, such as those operating in urban areas, with a duty cycle that does not yield high exhaust temperatures normally associated with regeneration.

Comparing the change in DPF back pressure during operation with a fuel containing mmt versus a fuel that does not contain the additive, the performance of the additive is apparent. This is illustrated in Figure 13. In this case, the engine was operated at a constant speed and load. The backpressure across the DPF increases as it loads up with soot. In the case for a fuel that is not additised, the soot oxidation occurs in the trap but much more slowly than the soot is being generated. The backpressure increase quickly and within 40 hours exceeds the engine manufacturer

back pressure limit. In the case where the fuel was additised with mmt, the soot oxidation rate is much higher than observed without the additive. The oxidation rate with additive approaches the rate of soot generation and DPF backpressure builds much more slowly. After more than 150 hours of operation on the additised fuel, the DPF back pressure has not come near the manufacturer's back pressure limit. An advantage of the higher soot oxidation rate is lower back pressure in the engine exhaust and improved fuel efficiency.

3.1.3. Gasoline Performance Additives

During the normal operation of a gasoline-powered vehicle, fuel related deposits tend to form on various fuel system components. When these deposits occur, fuel injectors can foul, leading to poor fuel delivery and volatilization that result in increased emissions and drivability problems. When deposits form on intake valves, interference with air fuel mixing takes place, resulting in increased emissions and loss of power and acceleration. Deposits also form in the combustion chamber leading to increased octane requirements and loss of performance, and in some cases, engine knock. In each of the above scenarios, deposit formation can also lead to increased fuel consumption.

Performance additives to control fuel system deposit problems have been around for over 50 years. Many early versions of gasoline additives were low molecular weight amine-based chemistries designed to keep carburetors clean and avoid carburetor icing. With the introduction of fuel-injected vehicles in the 1980s, the low concentration of additive needed to keep carburetors functioning was insufficient to keep injectors from fouling. While higher concentrations of these additives were effective in keeping fuel injectors clean, they also contributed to a growing problem caused by intake valve deposits (IVD). To control IVD, higher MW amine-based chemistry blended with mineral oil "carriers" became the predominate method for controlling fuel injector and intake valve deposits. In some cases, additive treat rates to effectively control intake valve deposits approached 1000ppm. These high concentrations soon led to significant increases in combustion chamber deposits and increases in engine octane requirements. As a result of the additives' inefficiencies, in the early 1990s, mineral oil carriers were phased out while synthetic carriers started becoming widely used in formulating gasoline performance additives (GPA) as we know them today.

Additive performance is dependent on additive chemistry, the type and level of carrier fluids used and overall treat rate. In the current additive market, a typical GPA will consist of, at a minimum, an active detergent component and a synthetic carrier. The carrier serves several functions in an additive package: 1) provide a fluid medium through which the detergent can disperse deposits precursors, 2) provide valve stick protection, and 3) not contribute to combustion chamber deposits. These packages may also contain demulsifiers, corrosion inhibitors, antioxidants, friction modifiers and octane improvers.

3.1.4. Port Fuel Injected Engines Cleanliness and Performance

Port fuel injected gasoline engines have been in the market for many years and represent the engine technology utilized in the large majority of the gasoline vehicles. To significantly reduce emissions and improve fuel economy, manufactures have worked to improve design and control of the engine, specifically to control the air to fuel ratio. Deposits in the fuel intake system can have detrimental impact on preparation of the air/fuel charge leading to sub optimal engine performance. Detergent

fuel additives, added to gasoline can work to remove previously formed fuel system deposits and restore vehicle performance, lowering emissions and improving fuel economy.

The performance of the gasoline detergent and its ability to clean-up fuel/intake system deposits in the standard M102E test is illustrated in Figure 14 for a number of different fuels including two reference fuels and a market fuel containing ethanol (E10). The severity of the three fuels differed, building different levels of deposits, but in all cases operation on gasoline containing a detergent additive provided significant clean-up of the valve deposits.

The gasoline detergent additives also deliver clean-up in vehicle operation, improving fuel efficiency and lower vehicle emissions. The effect of a gasoline detergent additive on valve cleanliness for three vehicles designed to meet stringent EU IV or US Tier 2 emission standards is illustrated in Figure 15. A detergent additive, at a fairly low commercial treat rate, reduced valve deposits by an average of almost 30%. The emission performance and fuel consumption of these vehicles was also measured before operation on the additised fuel and after the clean-up phase. As illustrated in 16, after operation of the additised fuel and subsequent IVD clean-up, average hydrocarbon, carbon monoxide and nitrogen oxide emissions from the vehicles were all reduced. While one of the vehicles in this test displayed most of the fuel economy improvement, there was an average of slightly greater than 1% improvement in fuel economy for the fleet after the fuel/intake system clean-up.

Controlling fuel system deposits can also help maintain a vehicles power and acceleration closer to new vehicle design. Figure 17 shows the benefit of cleaning up intake system deposits on vehicle power and acceleration. The power before and after clean-up, compared to a newly built engine is significant. The improvement with use of the gasoline additive cuts the average time required for the vehicles to accelerate from 100 km/hr to 145 km/hr from 4.87 seconds to 4.65 seconds. These examples illustrate the benefits of using gasoline fuel additives to keep clean or clean –up the engine intake systems.

3.1.5. Hybrid Valve Cleanliness

Unlike the port fuel injected gasoline engines discussed above, a gasoline hybrid vehicle uses its gasoline engine periodically. While the specific conditions under which the engine and electric motor operate are dependent on the design philosophy of the manufacturer, the engine for example, may be switched off during low speed operation or when the vehicle is at rest.

The period of time after an engine is turned off and remains hot is called a hot soak. The frequency of hot soaks can have a dramatic influence on the formation of fuel system deposits. During the hot soak, fuel is not flowing past the valve or through the injector. The fuel remaining on the valve or in the injector can break down to form deposits. Compared to an engine in a non-hybrid configuration, the hybrid engine experiences a greater frequency of hot soak and may show greater propensity to form fuel system deposits or alter the effectiveness of additives originally designed to provide fuel system cleanliness in non-hybrid vehicles.

The performance of two additives regularly found in gasoline was evaluated to determine the ability of the additives to control intake valve deposit. The work was performed using a 2007 Toyota Camry gasoline-electric hybrid vehicle powered by a combination of a 2.4L I4 engine and a 40 hp electric

motor running a 8,000 km driving cycle that consisted of urban, rural and highway components. This cycle resulted in numerous periods of hot soak. Four tests with different additive combinations and treat rate were performed: (1) no additives; (2) detergent at a typical commercial treat rate; (3) detergent at a premium treat rate of three times that used in (2); and (4) detergent at the typical treat rate used in (2) plus the octane enhancing additive mmt® at 8.3 mg manganese per liter.

As illustrated in Table 6, the fuel without additive resulted in the formation of an average of 192 mg of deposits per valve. Detergent at a typical commercial treat rate provided significant protection, with only 14 mg of deposit per valve while increasing the treat rate by a factor of three resulted in superior cleanliness with about 1 mg of deposit per valve. The fuel additive mmt is widely used in gasoline to increase octane and has been shown to provide enhanced valve cleanliness in non-hybrid vehicles. This enhanced cleanliness was also observed in the hybrid vehicle. In this case, the base fuel containing the detergent at the typical commercial treat rate and mmt provided the same superior performance as observed from the use of the detergent in the base fuel at three times the typical treat rate.

3.1.6. Direct Injection Gasoline – Injector Plugging

The direct injection gasoline (DIG) engine operates by injecting fuel directly into the combustion chamber and is capable of providing significantly improved fuel efficiency. The gains in fuel efficiency and ability to produce needed power are achieved through the higher compression ratio associated with charge cooling, the precise control over amount of fuel and injection timings which are varied according to the load conditions. The proper formation of the fuel/air mixture in the cylinder is important to ensure robust operation of engine overall operating conditions. Engine designers utilize wall guided and more recently, spray guided systems to ensure proper formation of a combustible fuel/air mixture and robust engine performance. Both of these approaches rely on proper operation of the fuel injection system. Formation of fuel injector deposits can adversely impact fuel spray formation and reduce levels of fuel injected into the engine impacting engine operation.

Fuel additives play an important role in maintaining the operation of DIG engines at optimal levels and preventing loss in performance. The injectors in the DIG engine are exposed to higher temperature than those used in the PFI vehicles discussed above, and are potentially prone to the formation of deposits that restrict flow and adversely impact performance. Injector manufactures design the injectors with the goal reducing the propensity for deposit formation, but often injector deposits will form.

Using a vehicle equipped with a four cylinder direct injection gasoline engine, the impact of deposit and the role of additives was demonstrated. The vehicle was operated over a period 48 hours at highway speeds and underwent periodic hot soaks. After this period of time the base fuel displayed about 9.4% loss in fuel flow through the injectors due to deposit build up.

Gasoline detergent additives can be used to provide various levels of performance versus the base fuel. Figure 18 show the relative performance of two different additive technologies at typical commercial treat rates. Both of these technologies provide good performance in PFI engines. However, one is designed to also provide protection against deposit formation in DIG engines. For reference, the performance of the fuel containing mmt is included in Figure 18. The fuel additive

mmt improved performance of the base fuel, resulting in almost a 33% reduction in flow loss compared to a base fuel without mmt.

4. SUMMARY

The focus on improving efficiency, fuel economy and reducing emission in the transport sector is driving changes to both fuels and engine technology. The fuel changes are taking the form of modification to fuels produced form petroleum sources and the increased use of alternative fuels. These fuel changes place new demands on the storage and distribution systems to ensure fuels can be effectively transported in a safe fashion and maintain their integrity. In addition, the fuels themselves may not possess the appropriate properties for use through the vehicle park.

There are a number of engine technologies that may be adopted alone or in combinations to improve efficiency and reduce emissions. While some of the changes in fuel properties are being driven by engine technical requirements, not all of the needs of new engine can be met by directly altering bulk fuel properties.

Fuel additives will play an increasingly important role as new fuel and engines technologies are introduced, ensuring the safe and effective transportation of fuel and to allowing for effective operation of changing engine technologies. Additives can help reduce vehicle emissions, improve fuel efficiency, drivability and allow engines to operate as designed. They provide refiners with production flexibility and a means to produce high-quality fuels. As they have for many years, fuel additive technology will continue to enable the formulation of fuels to meet specifications in a cost-effective manner, upgrade fuel quality and improve the overall performance in gasoline and diesel-powered vehicles.

Gasoline Property Change	Reason For Change	Impact on Gasoline Properties
Sulfur Reduction	- Improved aftertreatment performance -Reduced sulfur emission -Reduced olefins	-Loss of octane -Silver corrosion -Improver stability
Ethanol	-Added volume -Renewable fuel -Lower carbon footprint	Reduced mileage -Sulfate filter plugging -Phase separation -Corrosion -Increase octane -Currently incompatible with pipeline distribution in some parts of the world

Table 1. Selected Gasoline Changes, Reasons for Changes and Impact on the Fuels Properties

Diesel Fuel Property Change	Reason For Change	Impact on Diesel Fuel Properties
Sulfur reduction	-Aftertreatment -Reduced particulates -Reduced sulfate emissions	-Reduced lubricity -Improved stability -Improved cetane quality -Reduced conductivity -Higher cloud Point
Biodiesel/Blends FAME	-Renewable fuel -Volume -Particulate and NOx reduction	-Improved Lubricity - Degrade low temperature properties -Currently incompatible with pipeline distribution in some parts of the world.
Renewable diesel -Refinery processing oils and fats -Bio to liquids – Fischer Tropsch	-Derived from renewable sources	-Higher cetane quality -Higher cloud point -Lower lubricity

Table 2. Selected Diesel Fuel Changes, Reason for the Changes and Impact on the Fuels Properties.

Product Chemistry	Main Use
Hindered Phenol	Jet fuels (military and civilian), ultra-low-sulfur distillate fuels, relatively stable gasolines
Phenylenediamine (PDA)	Very unstable gasolines
Hindered Phenol/ PDA Mixtures	Most gasolines
Metal Deactivator	Military jet fuels, gasolines and distillate fuels with dissolved metals.
Hindered Phenol Dilutions	Refineries which cannot heat trace additive injection lines. Cold climates.
Amines and Dispersants	Unstable distillate fuels

Table 3 . Summary of Antioxidant and Stabilizer Chemistries Used in Fuels and Their Primary Applications.

	Cloud Point, ° C Bottom 20% of fuel after settling
Base Fuel (cloud -14° C)	1.1
+ CFI additive @ 1X	-10.9
+ CFI additive @ 2X	-13.4
+ CFI additive @ 3X	-13.8

Table 4. Impact of Wax Settling or Stratification on the Cloud Point of an ULSD with and without Additive Having WASA Performance.

Technology	Potential Cleanliness Challenge for Fuel Additives
Cam Phasing	Valve, injector, intake
Variable Valve Lift	Valve, injector, intake
Turbocharging	Hotter engine, EGR, intake
Cylinder Deactivation	Valve and injector
Variable Charge Motion	Intake system, charge motion device
Variable Compression Ratio	Intake
Gasoline Direct Injection	Injectors
Homogeneous Charge Compressed Ignition (HCCI)	New fuel, injector
Diesel – HSDI	Increased diesel use, injectors
Hybrids	Valve, injector, intake

Table 5. Potential Engine Technologies for Improved Fuel Economy and Potential Cleanliness Needs To Be Addressed Through Use of Fuel Additives.

Additive	IVD (mg)	IVD (% vs base)
Base(no additive)	192	-
Commercial Detergent	14	-92%
3X Treat Rate of Commercial Detergent	1	-99%
Commercial Detergent + MMT @ 8.3 mg Mn/l	1	-99%

Table 6. Intake Valve Deposits Formed in Gasoline Hybrid Vehicle Using Base Fuel and Base Fuel Containing Commercial Gasoline Additive at Two Treat Rates and Base Fuel Containing mmt and the Commercial GPA with.

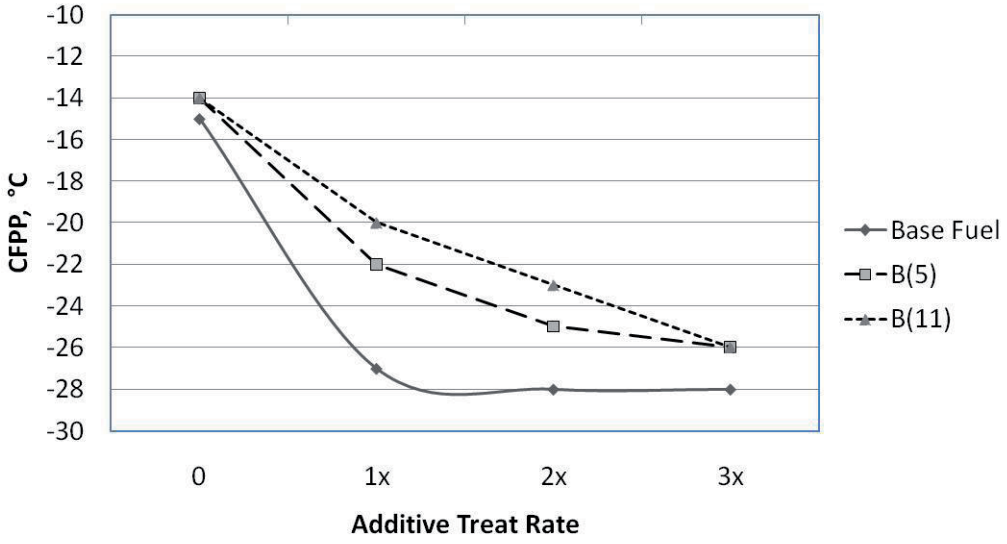

Figure 1. Average CFPP Response of 5 Base Fuels and Biodiesel Blends of the 5 Base Fuels and Soy Biodiesel Treated with 3 Levels of Cold Flow Improver.

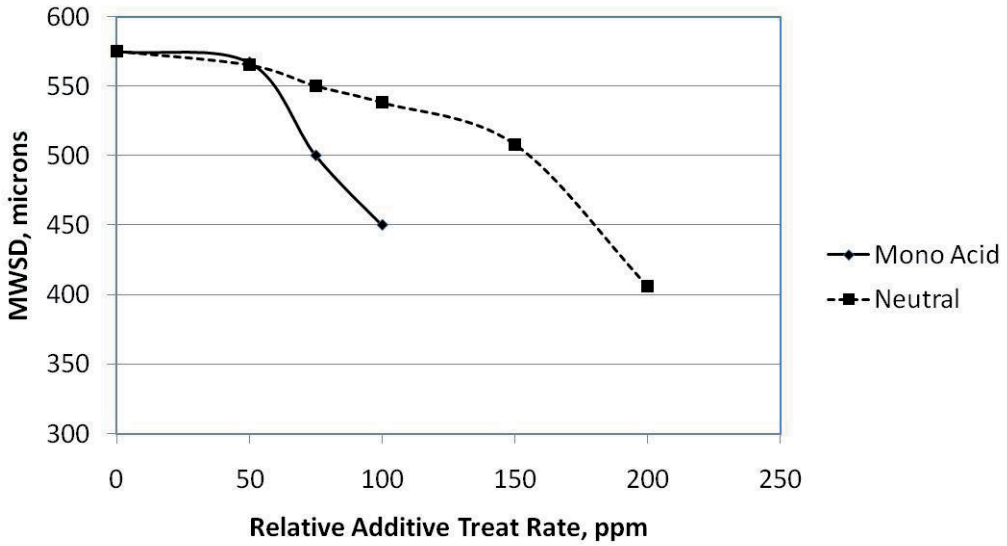

Figure 2. Mono-acid Lubricity Additive Comparison to Non-acidic (Neutral) Lubricity Additives.

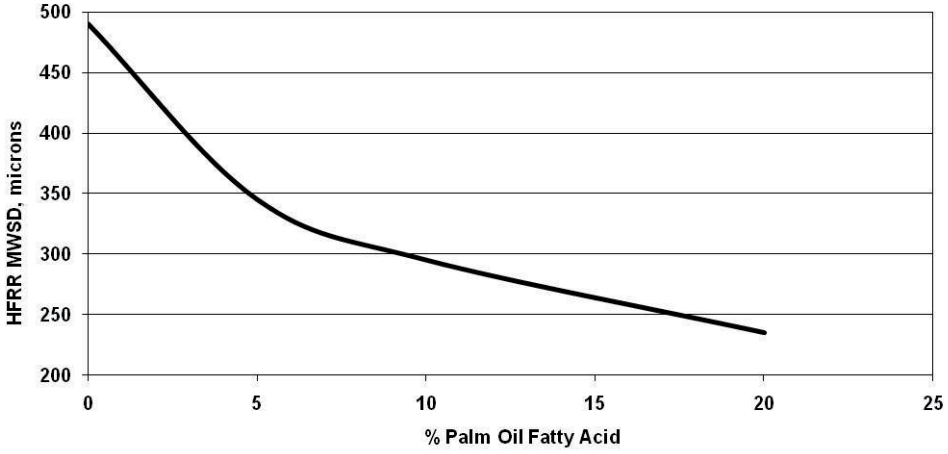

Figure 3. Effect of Palm Oil Fatty Acid Biodiesel on Lubricity of Diesel Fuel as Measured by HFRR.

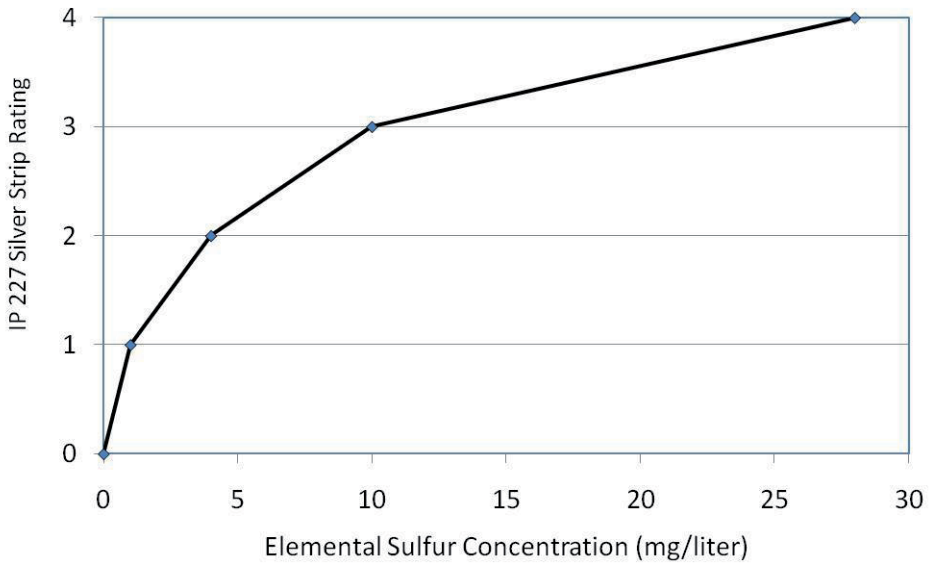

Figure 4. Effect of Elemental Sulfur on Gasoline Silver Corrosion Ratings. Silver Strip Immersed in Unleaded Regular Gasoline Inside Glass Test Tube Sealed in Stainless Steel Bomb at 50°C for 3 Hours.

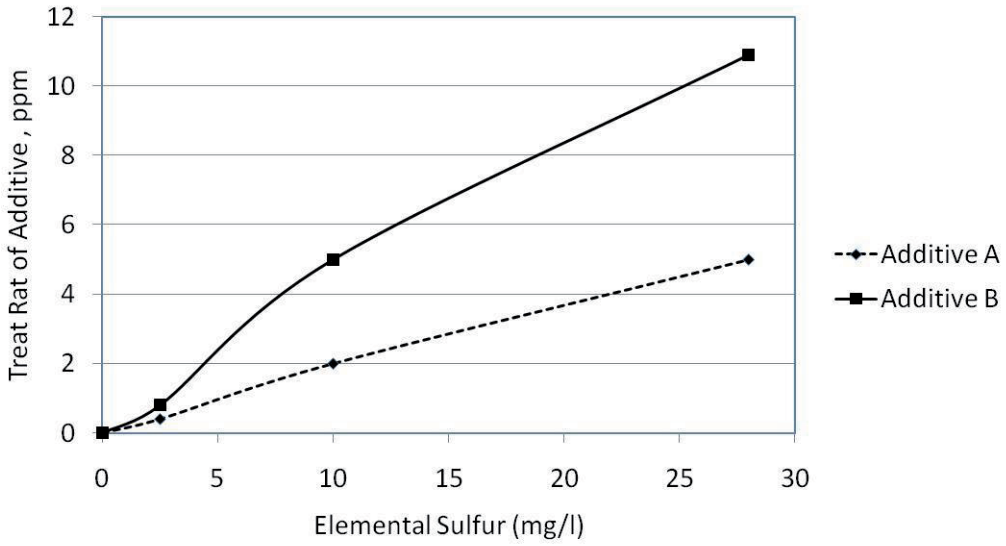

Figure 5. Treat Rate of Two Different Corrosion Inhibitor Additives Needed to Achieve Zero Silver Strip Rating for a Given Concentration of Elemental Sulfur in Gasoline.

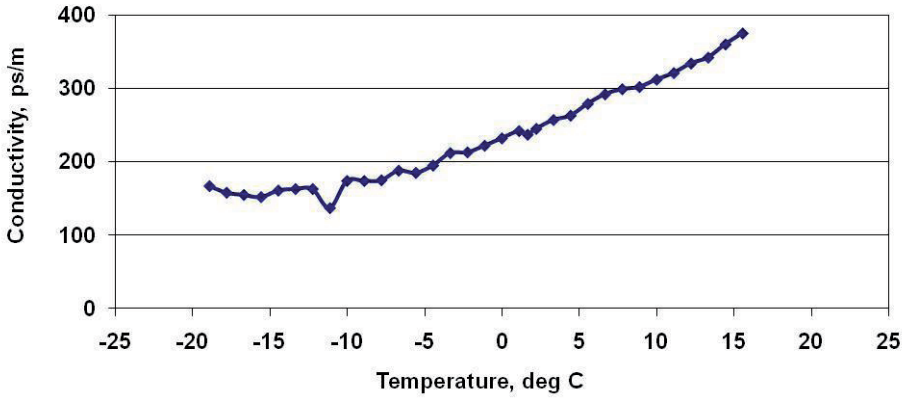

Figure 6. Fuel Conductivity Decreases with Fuel Temperature.

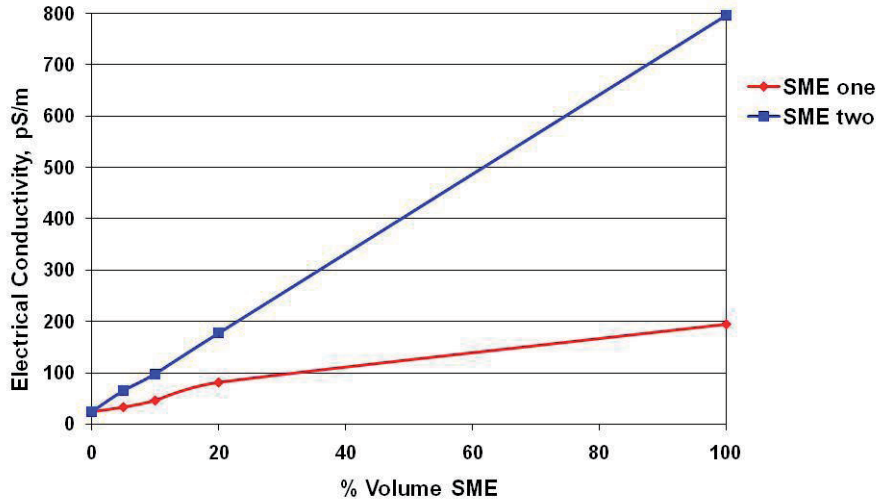

Figure 7. Conductivity of Biodiesel Blends as a Function of Biodiesel Concentration for SME from Two Different Sources.

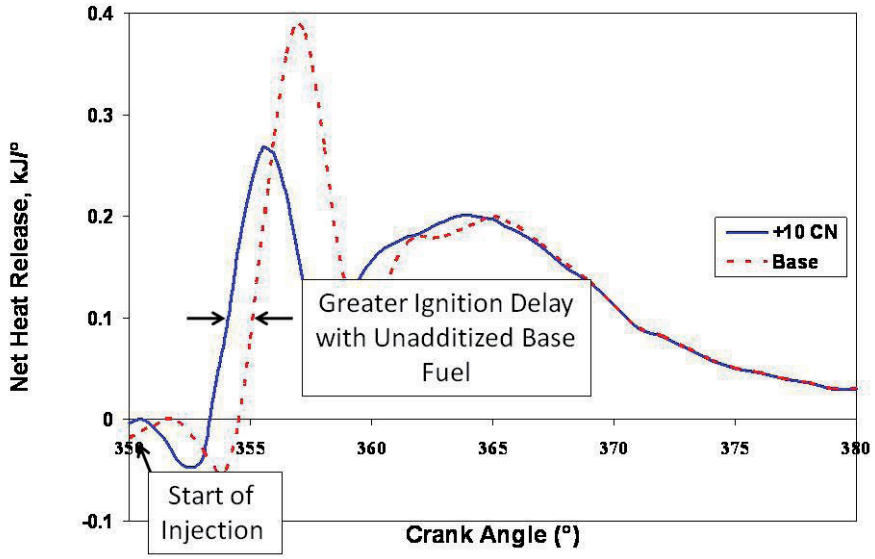

Figure 8. Reduced Ignition Delay For Diesel Fuel with 10 Cetane Number Increase (+10CN) Compared to Base Fuel.

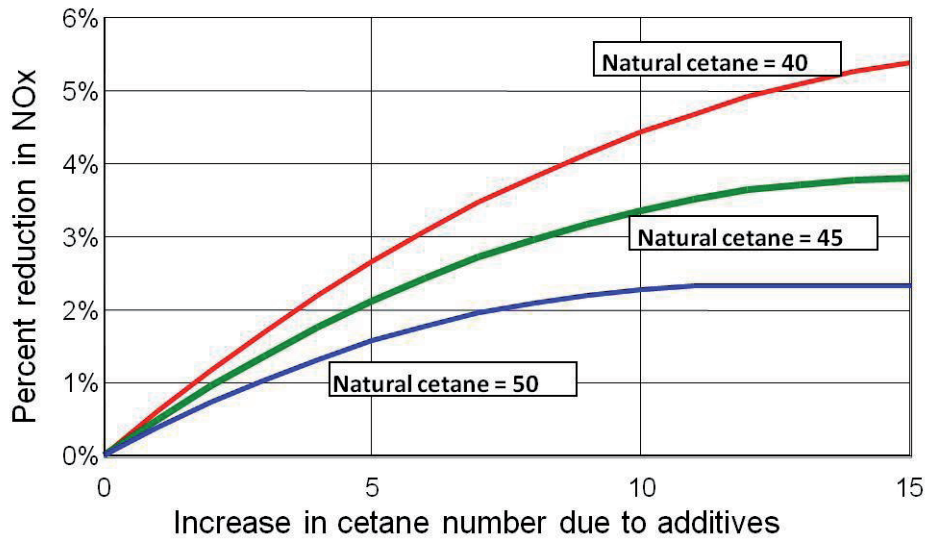

Figure 9. Change in NOx Emissions From Diesel Engine as Function of Cetane Number Increase For Fuels with Different base Cetane (Source US EPA).

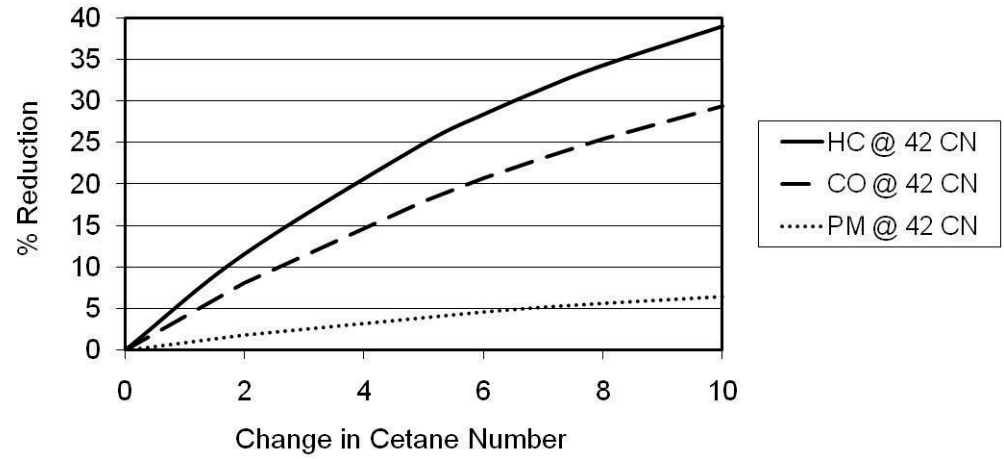

Figure 10. Change in CO, HC and Particulate Emissions with Change in Cetane Number for Fuel with Base of 42 Cetane (Source US EPA).

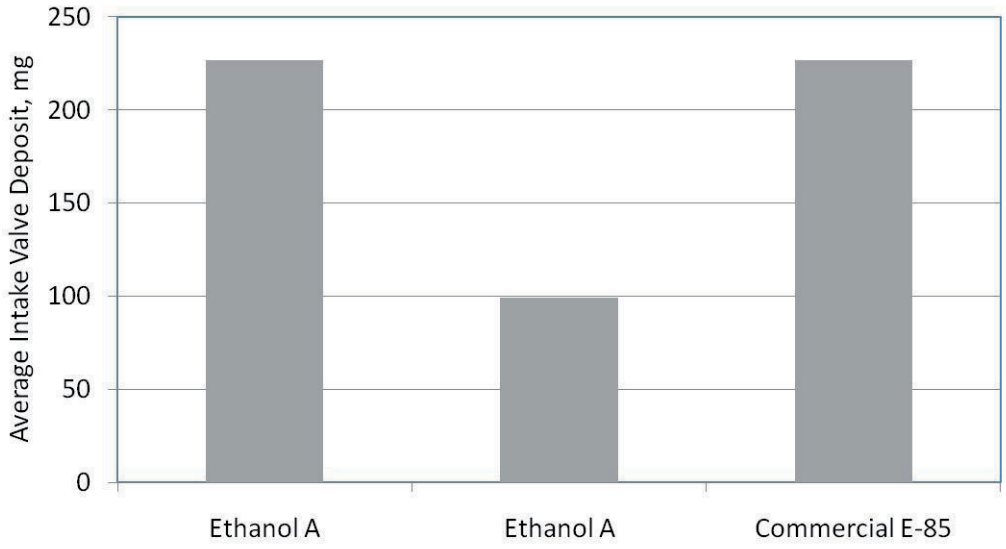

Figure 11. Differences in Intake Valve Deposit Forming Tendencies of E-85 Fuel Made from 2 Fuels Grade Ethanol Sources and Commercial E-85. Tests Conducted in a 2007 GM Flexible Fuel Vehicle Operating for 5000 Miles.

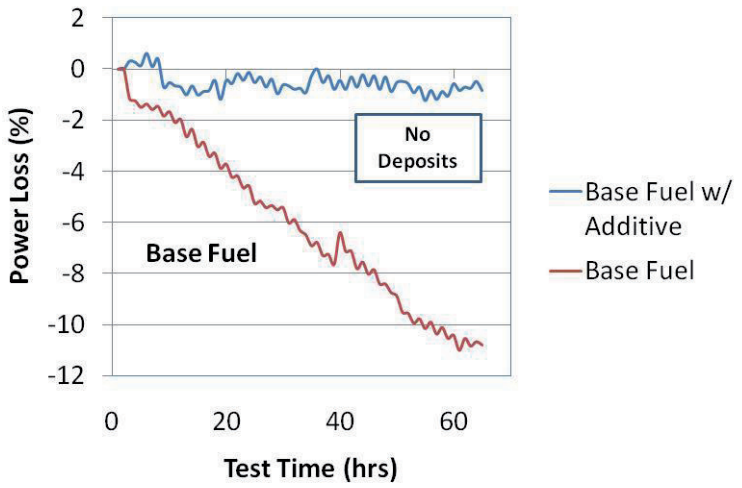

Figure 12. Power Loss Due to Injector Coking in High Speed Direct Injection Engine Test (DW10) for base Fuel and Base Fuel Containing Diesel Additive.

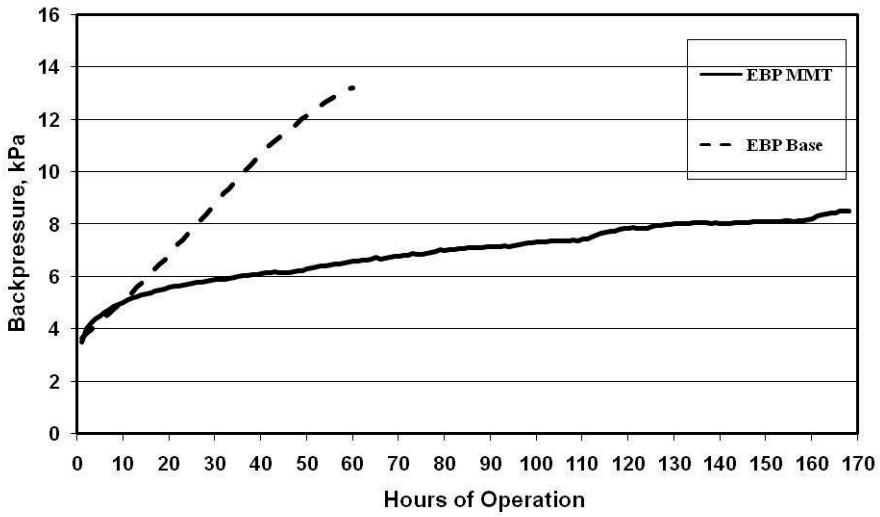

Figure 13. Exhaust Gas Back Pressure (EBP) During Steady-State Diesel Particulate Filter Loading Using Base Fuel and Base Fuel Containing mmt.

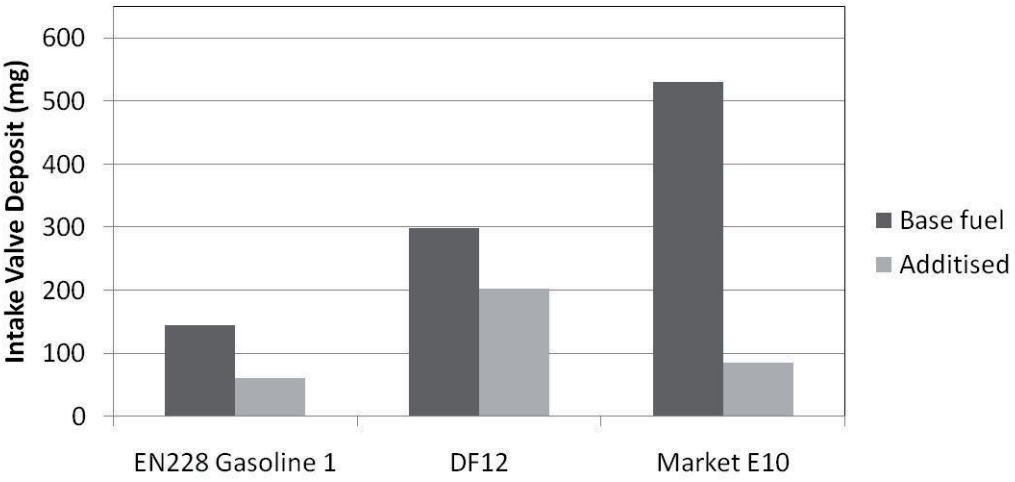

Figure 14. Intake Valve Deposit Clean Up Using Base Fuels Containing Gasoline Additive in M102E IVD Test. Clean Up Is of Deposit Built Form Base Fuel. Examples for Three Different Base Fuels.

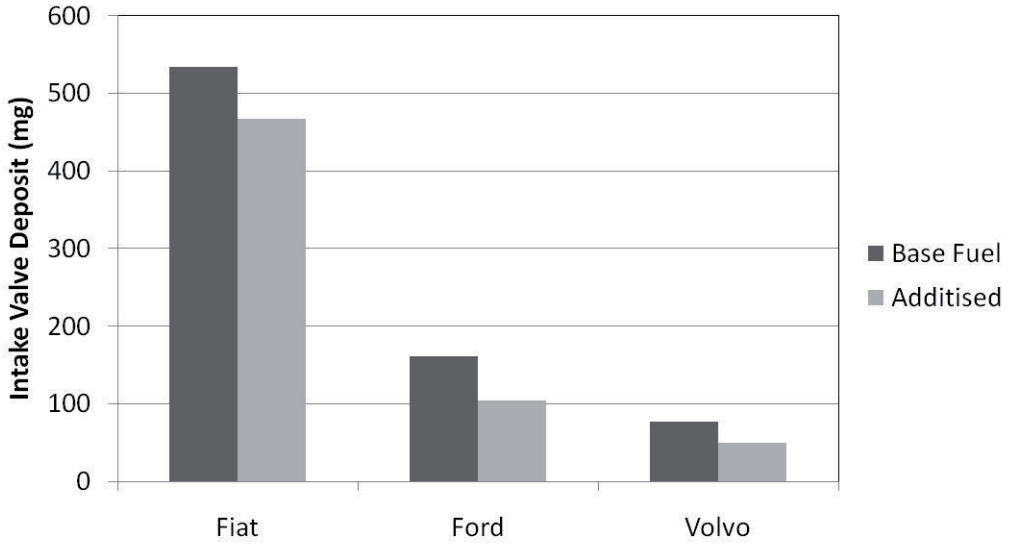

Figure 15. Intake Valve Deposit Clean Up Using Base Fuels Containing Gasoline Additive in Three Vehicles. Clean Up Is of Deposit Built Form Base Fuel.

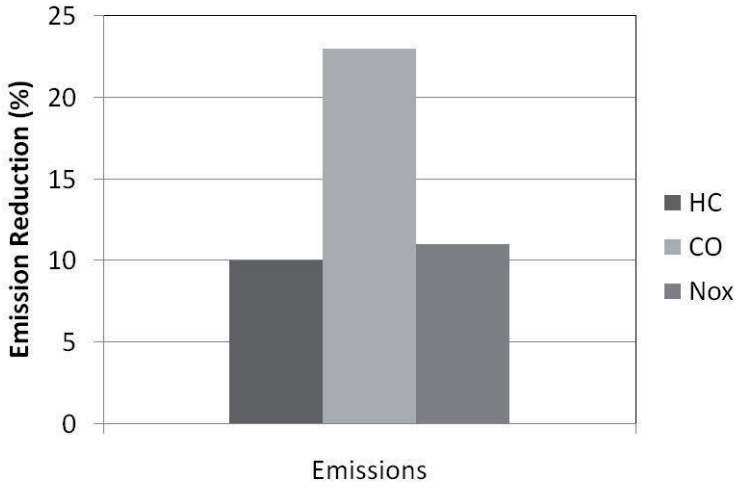

Figure 16. Average Emission Reduction Achieved After Clean Up For Three Vehicles.

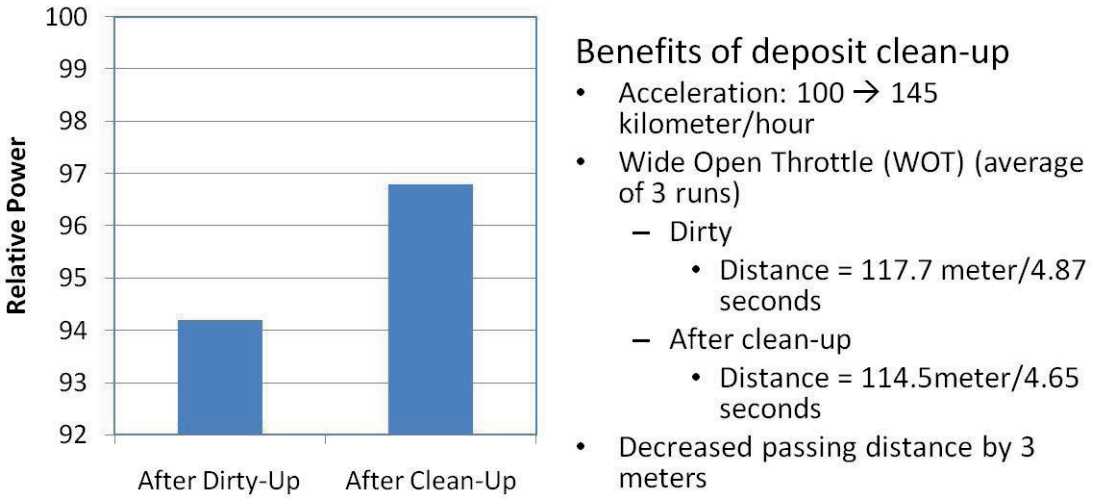

Figure 17. Improvement in Power and Acceleration on Cleaning up Fuel System Deposits. Average of Four Different Vehicles. Dirty-up for 8000 km on Commercial Gasoline and Clean-up for 2400 km on Premium Level of Additive in Regular Unleaded Gasoline.

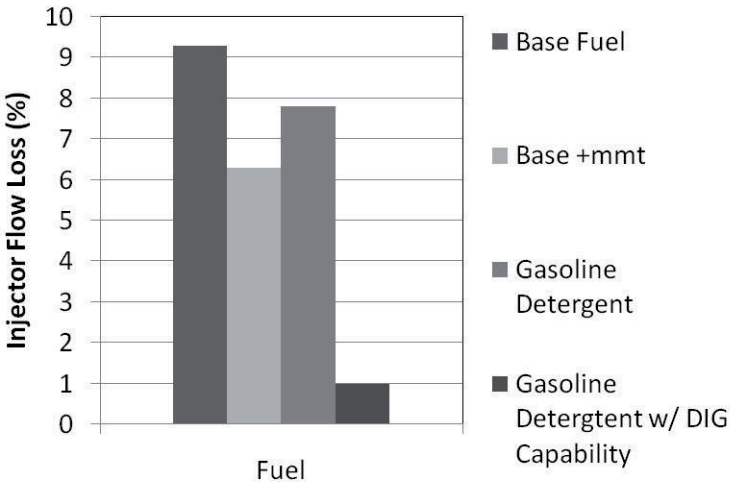

Figure 18. Cleanliness Performance of Additives in Direct Injection Gasoline Engine.