

A General Method for Fouling Injectors in Gasoline Direct Injection Vehicles and the Effects of Deposits on Vehicle Performance

Charles S. Shanahan Afton Chemical Corporation

S. Scott Smith Afton Chemical Corporation

Brian D. Sears Afton Chemical Corporation



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ABSTRACT

The ubiquity of gasoline direct injection (GDI) vehicles has been rapidly increasing across the globe due to the increasing demand for fuel efficient vehicles.

GDI technology offers many advantages over conventional port fuel injection (PFI) engines, such as improvements in fuel economy and higher engine power density; however, GDI technology presents unique challenges as well. GDI engines can be more susceptible to fuel injector deposits and have higher particulate emissions relative to PFI engines due to the placement of the injector inside the combustion chamber. Thus, the need for reliable test protocols to develop next generation additives to improve GDI vehicle performance is paramount.

This work discloses a general test method for consistently fouling injectors in GDI vehicles and engines that can accommodate multiple vehicle/engine types, injector designs, and drive cycles, which allows for development of effective GDI fuel additives.

A key factor to the versatility of this test protocol is the test fuel formulation, which uses added chemical accelerants to mimic the fouling effects of fuel aging and sulfur accumulation in the injector nozzle. The test fuel formulation serves to accelerate the fouling potential of fuels that are already capable of dirtying-up fuel injectors on their own without chemical accelerants and allows real-world fuels to be evaluated for fuel additive performance within more reasonable test times. This test method was also complimented by emissions and fuel economy measurements in order to quantify the negative effects of injector fouling on vehicle performance and the opportunity for DCAs to help prevent these problems.

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INTRODUCTION

As the percentage of GDI vehicles continues to increase worldwide, in some markets overtaking PFI cars as a percentage of new cars manufactured, [1] the industry is becoming increasingly aware of the challenges presented by this technology.

[2] For example, fouling of the injectors of GDI vehicles can lead to a deterioration in fuel economy [2a] and an increase in harmful emissions. [2b] The good news for the industry is that these problems are, in part, deposit related and can be mitigated by the appropriate fuel additive. In many cases, however, the appropriate fuel additive for the job may not be the conventional PFI detergent system.

Thus, in the absence of industry standard GDI test methods, the market is largely lacking appropriate additives to solve this unique challenge.

In order to understand and address the problems presented by emerging GDI technology, Afton has a long history of GDI test development [3] and collaborative GDI research ultimately aimed at developing solutions that benefit the consumer and the environment. Almost twenty years of research has facilitated the development of reliable and general methods for GDI vehicle testing, which has provided a platform to develop effective additive solutions for this critical vehicle platform.

RESULTS & DISCUSSION

RAPID INJECTOR FOULING TEST (RIFT) METHOD DETAILS

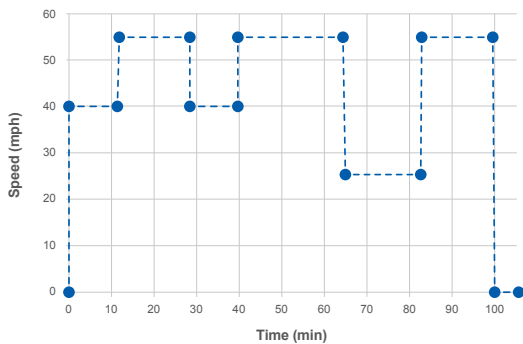
The foundation for much of Afton's GDI research is based on the use of a modified Quad-4 drive cycle (Graph 1), [3] which has shown considerable generality in encouraging rapid fouling of injectors in GDI vehicles when the gasoline used has endogenous dirty-up properties. While some studies have attempted to qualitatively identify the features of a fouling gasoline [4] (i.e. distillation properties, aromatic/olefin content, sulfur levels, etc), there is still not a clear understanding of what causes gasoline to reliably cause deposit formation in and on the fuel injector of GDI vehicles. Consequently, identifying an appropriate fouling test fuel is principally the work of trial and error.

In order to measure fouling in vehicle testing under these conditions, there are a number of different options available. Direct measurements of injector fouling can include visual inspection of the injector, fuel flow analysis and fuel spray analysis. These methods, however, are invasive and require the injectors to be

removed from the vehicle/engine either during or after the test is complete. Injector removal carries with it the risk of disturbing the deposits and may therefore lead to less accurate results regarding the level of deposit formation during the test and any subsequent additive response to that deposit. These techniques allow for less data over the course of the testing (usually only one data point at SOT, MOT, and EOT), which inherently leads to lower statistical confidence in the conclusions that are made from the data. However, having the option to corroborate real-time data with visual or spray analysis can be a powerful method for understanding deposit formation mechanisms.

[2c,4] Indirect measurements of injector fouling such as injector pulse width (IPW) or long term fuel trim (LTFT) are preferable for routine analysis of injector fouling because both can be attained from the engine control unit (ECU) and provide modal, real-time data as the testing progresses. Prior studies of how LTFT and IPW correlate to injector deposits (internal and external) have been reported and provide clear evidence of the connection.

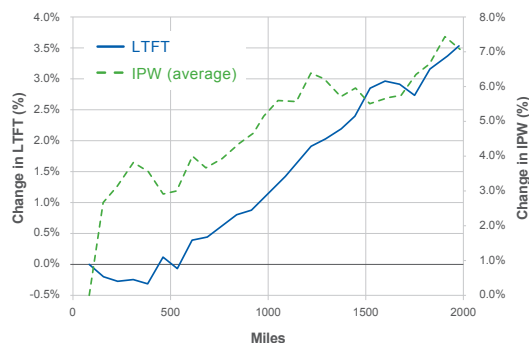
[3] Furthermore, the sheer volume of data made available by these measurements consequently leads to higher levels of statistical confidence in the data. Of the two, LTFT is generally easier to obtain from the ECU and does not require additional hardware, which sometimes IPW requires and LTFT generally has a higher signal-to-noise ratio than IPW.



Time (min)	0	0.5	11.75	11.95	28.35	28.55	39.5	40	64.5	64.75	82.75	83	99.4	100	105
Speed (mph)	0	40	40	55	55	40	40	55	55	25	25	55	55	0	0
Acceleration (mph/sec)		1.3		1.3		-1.3		0.5		-2		2		-1.5	
Steady State Duration (min)			11.25		16.4		10.95		24.5		18		16.4		5

Graph 1. Quad 4 Drive Cycle, Set Points, & Transitions

[3e] In comparing these metrics during the described test protocol (Graph 2), a strong directional correlation between IPW and LTFT over extended test time (>1500 miles) is observed. Furthermore, most vehicles are set to trigger a malfunction indicator lamp (MIL) if the LTFT reaches 25%, hence, LTFT most closely corresponds to what the driving public would ultimately interact with.



Graph 2. Comparing LTFT to IPW as Measures of Injector Plugging during a Single Test Run

The data in Graph 2 was collected on a 2013 Kia Optima (naturally aspirated 2.4L GDI vehicle on a mileage accumulation dynamometer).

The Kia Optima has proven to be an effective test platform due to the vehicle's current global market relevance, the ease with which the vehicle can be turned around between tests and maintained, and the high repeatability of its response to injector fouling conditions. The injectors are easy to remove for middle-of-test (MOT) or end-of-test (EOT) analysis (if desired) and the vehicle has provided very reliable data over different model years.

Over the course of testing fuels/additives by this method, the condition of the injectors cannot be overlooked. New injectors are broken in for 2000 miles before testing and an injector set is reused by cleaning the injectors in a sonication bath with a cleaning solution between tests.

Due to the increase wear and tear of turning over and cleaning the test hardware for multiple tests, the maximum recommend lifetime of a set of test injectors for this method is ~60,000 miles because, beyond that point, injectors may begin shifting mild and thus the data beyond 60,000 miles under RIFT conditions do not always correlate to earlier data points.

Intake system	Naturally aspirated
Engine size	2.4 L
Cylinders	Inline 4
Horsepower	192 hp @ 6300 rpm
Torque	181 ft-lbs @ 4250 rpm
Valve Timing	Variable
Valves	16

Table 1. Kia Optima Engine Specifications

CHEMICAL FOULING ACCELERANTS

Due to the sporadic fouling ability of test fuels in GDI vehicles, a program was initiated to screen readily available chemicals that could be added to gasoline to accelerate the dirty-up of injectors and shorten overall test times to reasonable and economical durations.

The result of that study was the development of the "acceleration cocktail" discussed herein that can be added to severe fuels to reliably increase the rate of dirty-up in GDI vehicles/engines. While screening for appropriate accelerants, chemical streams that met the following criteria were prioritized:

1. Represented naturally occurring chemical components in fuels
2. Did not significantly affect the chemical nature of the final injector deposit relative to those that were produced directly by market fuels

3. Were capable of accelerating the deposit formation of fuels that were already capable themselves of dirty-up
4. Were non-metallic
5. Were commercially and readily available for continued use if chosen

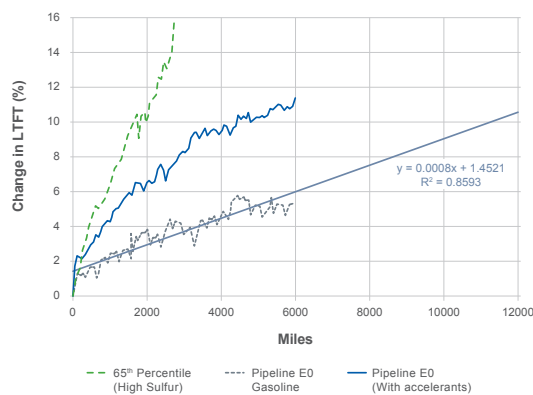
In previous studies, it was shown that elevated sulfur and certain nitrogen-containing molecules may lead to increased rates of injector fouling (Graph 3 - green dotted line) and thus numerous organic olefin, aromatic, heteroaromatic, and sulfur-containing compounds that represented constituents in gasoline were evaluated for commercial and economic viability, and di-tert-butyl disulfide (DTBDS), 2-methylindole (MI), and 4-methylbenzenethiol were chosen as strong candidates to be used as fouling accelerants.

Fuel aging is also known to lead to higher levels of severity and thus peroxides were evaluated in order to mimic fuel ageing affects. The base fuel consistently used for GDI testing is a Gulf Coast refinery gasoline that is capable of fouling injectors to about 6% LTFT in 6000 miles (Graph 3 - grey dotted line), which has approximately four times less fouling ability than a comparative high-sulfur 65th percentile fuel.

The base fuel result with the refinery E0 gasoline helps to define the upper limit of the real-world problem of injector fouling for which an accelerated test can be compared to. While not all fuels and/or vehicles in the field will be problematic with respect to injector fouling, in certain scenarios the correct combination of fuel and hardware could lead to significant fouling of the injector and potential loss in fuel economy, power or increases in harmful emissions. The refinery E0 gasoline case (Graph 3 - grey dotted line)

would represent such a scenario and is helpful for defining the real-world problem consumer's face.

The most rapid injector fouling in the field is therefore likely to be a 10,000-15,000 mile problem, but certainly this is well within the lifetime of the injector hardware. While valuable to quantify the field problem associated with injector fouling, a 10,000-15,000 mile dirty-up is not economically viable when it comes to evaluating and developing next-generation fuel additives. It is for this reason that a method for accelerating the native fouling properties of base gasolines is needed.



Graph 3. Base Fuel Dirty-Up versus Base Fuel with Accelerants

In order to accelerate the dirty-up of the refinery base fuel (Graph 3, grey line), a combination of di-tert-butyl disulfide (DTBDS, 409 ppmw, contributing 147 ppmw active sulfur to the fuel) and tert-butyl hydrogen peroxide (TBHP, 286 ppmw) were added to the base fuel and the dirty-up was accelerated to provide almost twice the rate of dirty-up relative to the base fuel alone (Graph 3 - blue solid line). Addition of this In fact, by comparing the accelerated dirty-up to the base fuel case, a 10% dirty-up in the accelerated case would correspond to a ~11000 mile problem in the base fuel case (calculated

from the extrapolated linear trend-line, Graph 3), which ultimately cuts overall test time by almost 7000 miles (~155 test hours). Shortening the overall test time not only lowers vehicle wear and tear during fuel/additive development programs, but decreases the likelihood of environmental changes that can influence test outcomes.

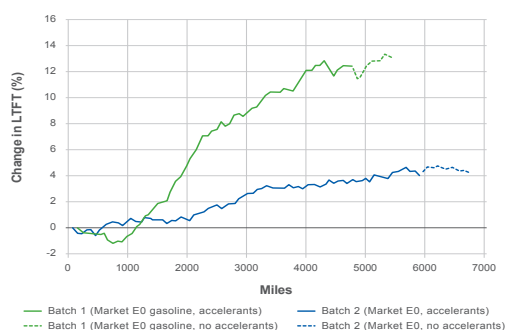
The chemical dopant blend was developed by systematic studies of the effects of the individual chemical accelerants on the dirty-up rate of the base fuel. In development studies, DTBDS alone provided a ~44% increase in fouling relative to base fuel and TBHP provided ~21% increase in fouling relative to base fuel. Various other accelerants (i.e. indoles, benzethiols, etc.) were also screened, however only DTBDS and TBHP provided statistically significant increases in base fuel fouling rates. In order to validate the results from this accelerated fouling method, it was important to scrutinize the chemical nature of the deposits that were formed from the doped and non-doped case.

The rationale for adding these accelerants was that high sulfur fuels have been shown to naturally accumulate in the nozzle deposits of the injector of even low-sulfur base fuels (according to SEM-EDX of the injector deposit, see Appendix), thus suggesting that organosulfur compounds/aggregates are in some way associated with deposit formation or deposit initiation. When the base fuel is doped with extra sulfur (as described above) the final deposit (compared to base fuel after 2000 miles) does not contain disproportionately more sulfur contribution to the deposit than is seen in the base fuel (see supporting information); therefore, DTBDS doping of the fuel appears to lead only to an acceleration of the deposit formation and not a fundamental change in the nature of the deposit.

Concurrently, the addition of TBHP is meant to accelerate fuel aging effects, which are also known to lead to increased fuel severity. The combination of both accelerants in the final fuel blend leads to reliably fast formation of carbonaceous injector deposits that represent real-world deposits formed under reasonable driving conditions. Therefore, the RIFT method presented is a realistic and economical tool for fuel and/or additive evaluation.

To further bolster the notion that the deposits formed from the accelerated fuel blend are representative of the real-world, the stability of the deposits formed in the injectors over the course of the test were analyzed. A weak deposit would ultimately be capable of being washed away by fuel alone and would not represent a real-world deposit. As demonstrated in Graph 4, when the acceleration cocktail was removed from the fuel following a dirty-up, and the vehicle was allowed to continue operation for an additional 1000 miles, the vehicle did not begin to clean-up on the base fuel alone. Without the accelerants present, the deposit formation either stabilized or deposits continued to form.

This provides further evidence that DTBDS and TBHP are not the cause of the deposit formation, but act solely as a catalyst to increase the rate of deposit formation in the test by possibly providing more of the binding elements of the deposit or by helping seed initial deposit formation.



Graph 4. Fuel Batch Variability and Deposit Stability (Accelerated Market E0 Gasoline, Batch 1 and 2)

TEST FUEL SEVERITY & TREATABILITY

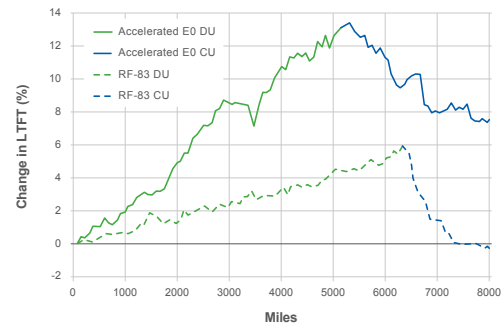
Over the course of hundreds of GDI vehicle/engine tests on various different base fuels, considerable swings in severity have been observed of the fouling ability of the final fuel blend as well as the apparent treatability of the fuels, which often are not mutually exclusive.

Batch to batch variation of the base fuel severity and treatability on the same refinery stream (Graph 4) can lead to levels of fouling as low as 4-5% LTFT to levels over 15% LTFT in fewer than 6000 miles. For this reason, an assessment of base fuel severity (BFS) and base fuel treatability (BFT) is essential in order to properly compare fuel and additive performance when switching to a new batch of test fuel.

Without this analysis, two samples cannot easily be compared. For example, Graph 5 shows the result of two subsequent dirty-up/clean-up tests on the same Mannich-based DCA, at the same treat rate, in the same vehicle, but on two different fuels (see supporting information for comparative fuel analysis). Using the RIFT method with the accelerated fuel blend, a 13% dirty-up and about 52% clean-up in 2964 miles is achieved, whereas using the RIFT protocol with RF-83 you see 6% dirty-up and 100% clean-up in less than 1000 miles. In this case, the bulk fuel specifications of RF-83 and the accelerated fuel blend are very similar, and it is not immediately obvious that there should be such a dramatic difference in severity and treatability.

If two additives were being compared, each tested in a different fuel; one would naturally conclude that the result in the RF-83 case is that of a higher performing additive. In this case, however, the

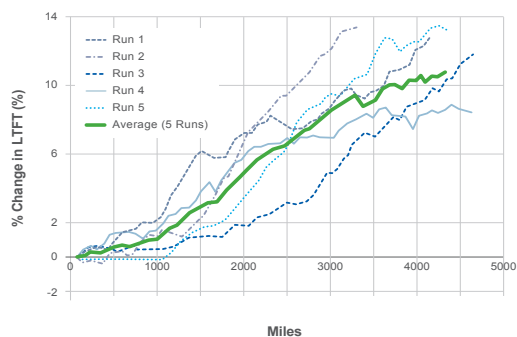
additives are the exact same, which is why it is recommended that additives are compared using a standard method on the same batch of test fuel for the most precise appraisal possible.



Graph 5. Comparing Test Fuel Severity and Treatability by Mannich-Based DCA (Accelerated Refinery Gasoline, Batch 2 versus RF-83)

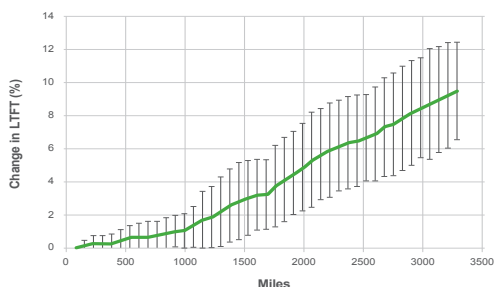
TEST METHOD REPEATABILITY AND STATISTICAL ANALYSIS

Using a 2014 Kia Optima vehicle and the accelerated fuel blend on the Quad 4 drive cycle, the RIFT method's overall repeatability in dirty-up mode was evaluated. Graph 6 shows five subsequent dirty-up runs on the same set of injectors (cleaned between each test), as well as the average of all five runs (solid green line). On average the dirty-up exceeds 10% LTFT in ~4000 miles of testing. Comparing these data to that in Graph 3, this batch of test fuel has about the same level of dirty-up severity as in the prior analysis; therefore the results in Graph 6 could be said to reliably simulate an 11000-12000 mile problem in this vehicle in under four days of test time.



Graph 6. Test Method Repeatability with Accelerated Fuel Blend (Market E0 Gasoline, Batch 2)

Statistical analysis of this dataset (Graph 7) clearly shows that at >1400 miles of testing (or >2.5% LTFT) one can be 99% confident that the injectors have fouled to a point that is statistically above the baseline. This means that keep-clean testing can be done with very short test times in order to assess an additive's performance relative to the base fuel. Furthermore, clean-up testing can be confidently begun any time after this point, however, longer test durations allow for more discrimination of additive performance in clean-up mode.



Graph 7. Statistical Analysis of Test Repeatability applying a 99% Confidence Interval

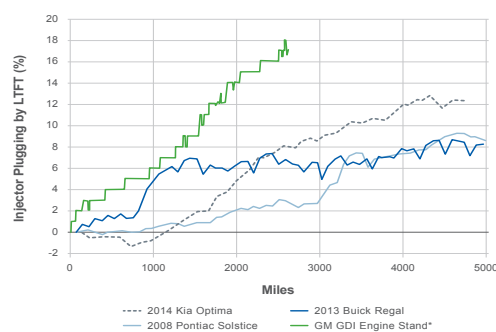
FLEET RESPONSE TO RIFT METHOD

One of the powerful aspects of this RIFT method is not just the reliability and repeatability, but the generality of this approach as it applies to multiple vehicle makes and models.

This method has been applied to a large variety of different GDI vehicle makes/models with good success. Not every vehicle make/model tested responded in a reliable way; however, most GDI vehicles will respond in some fashion but to varying degrees depending on vehicle make/model.

Some vehicles, however, are better test platforms than others and Graph 8 shows the response of three different test vehicles to this RIFT protocol using the accelerated fuel blend method. All three vehicles responded similarly to the 2014 Kia Optima providing $\geq 8\%$ dirty-up in ~4000 miles of testing.

This fleet well represents modern GDI vehicles by including engines containing hardware from two of the major fuel-system management suppliers.



Graph 8. Fleet Response to RIFT Method (Accelerated Market E0 Gasoline, Batch 2)

The fuel doping method was also applied to a GM 2.0 L Ecotec engine on stand, which is the same engine present in the 2013 Buick Regal that was also tested in this study (Graph 8). This engine test, in this case, was performed under steady-state conditions at the speed/load set points of the 2013 Buick Regal vehicle at the 55 mph portion of the Quad-4 cycle previously described in Graph 1.

This approach was taken in order to determine if the dirty-up could be further

accelerated under steady-state conditions to consequently make the RIFT method even more economical.

Steady-state conditions are known to produce more rapid deposits due to the lack of acceleration transitions during the test. To that end, dirty-up on the engine stand proved to be considerably more rapid operating under steady-state conditions as the accelerated fuel blend was capable of fouling the injectors to >17% LTFT in 48 hours (compared to about 7% LTFT in the vehicle over a similar mileage).

The test time was translated to miles by multiplying test hour (48 h) by 55 mph in order to be transposed onto the same x-axis as the vehicle data. The comparison of the steady-state engine test to the transient vehicle test exemplifies the difference in approach of the RIFT method to other accelerated methods in the literature.

Ultimately, two approaches can be taken to accelerate injector fouling and thus reduce overall test times:

Approach 1

Modify engine hardware or operating parameters to create harsh operating conditions that accelerate injector fouling:

- A.** The benefit of this approach is that the harshness of the operating conditions can be used to produce fouling in a wider variety of test fuels and even mild market fuels that would otherwise not be responsive to injector deposit testing.
- B.** The drawbacks of this approach are that, in some cases, the operating conditions may not represent real-world driving conditions, which could introduce artifacts that would require a certain type of deposit control additive that may not mitigate real-world deposit formation.

Approach 2

Modify fuel properties to accelerate injector fouling by chemical means (the disclosed RIFT method):

- A.** The benefits of this approach are manifested in the ability to adjust the method to work in multiple vehicle makes, models, engines-on-stand, and real world driving conditions. This method is also widely adopted by industry standard tests. However, contrasting Afton's method to other industry fuel-doping procedures, dopants here can be utilized that represent native elements of the base gasoline (as described herein) and that ultimately form real-world representative deposits.
- B.** The drawbacks of this method are that mild market fuels will often not result in injector fouling in a vehicle under real-world driving (at least within reasonable test times) and therefore test fuel options are more narrow.

QUANTIFYING THE EFFECTS OF INJECTOR DEPOSITS ON VEHICLE PERFORMANCE

In order to understand and quantify the effects on vehicle performance of injector deposits created under the disclosed RIFT protocol, a compliment of emissions and fuel economy testing can readily be adapted to the disclosed GDI test method. When this type of data is desired, a test vehicle is subjected to emissions and fuel economy testing by following a standard emissions protocol on the clean vehicle, after dirty-up, and after clean-up if desired.

At each desired test point, the performance testing was repeated five times (with cold soaks before each data FTP-75 data point) and a 95% confidence interval was

CONCLUSIONS

applied to the data to quantify the effects of deposits on performance with high statistical confidence. The data from each bag was weighted per the EPA protocol.

Table 2 illustrates the effects of injector fouling following the RIFT protocol, where an LTFT of ~6% was achieved (representative of ≥ 6000 miles of regular operation on a harsh market fuel, refer back to Graph 3).

At this level of fouling, a significant increase in gaseous & particulate emissions are clearly observed, which are harmful to the environment and air quality. Furthermore, a significant loss in fuel economy is observed by both emissions and volumetric-based measurements of greater than 1. These problems being the result of injector deposit formation would therefore be benefited by a deposit control additive that could prevent or clean-up the harmful deposits formed by the base fuel under normal vehicle operation.

FTP-75 (Bag Weighted)	SOT (New)	EOT (Dirty)	% Change
THC [g/mi]	0.0675	0.0791	+17.2
CO [g/mi]	2.4756	4.2662	+72.3
NO _x [g/mi]	0.0476	0.0671	+40.9
CH ₄ [g/mi]	0.0304	0.0353	+16.3
Particulate Mass [g/mi]	0.0069	0.0111	+62.2
Emissions Based Fuel Economy (mpg)	28.741	28.293	-1.6
Volumetric Meter Based Fuel Economy (mpg)	28.546	28.237	-1.1

Table 2. Effects of Injector Fouling (6% change in LTFT) on Vehicle Performance (5 repeats on FTP-75 cycle applying a 95% Confidence Interval)

Leveraging over twenty years of GDI test experience, a reliable and general injector fouling method has been developed that accelerates the dirty-up of gasolines already capable of fouling injectors under real-world driving conditions.

The use of DTBDS and TBHP are benign fuel dopants that mimic sulfur and fuel-aging induced fouling mechanics and are capable of at least doubling the rate of fouling of the base fuel stock.

The chemical nature of the deposit formed under these conditions is not significantly different to that formed under real-world conditions and statistically significant injector fouling in a vehicle can be accomplished in less than 1500 miles (or less than 36 hours) following the RIFT protocol.

It was also shown that a significant increase in gaseous & particulate emissions and decrease in fuel economy occurs as a result of GDI injector fouling. Thus, the use of fuel additives capable of mitigating injector deposits could be a valuable way of improving environmental air quality and improving vehicle performance for the consumer.

The general RIFT method that has been developed by Afton has consequently proven to be a rapid and reliable way to develop deposit control additives with high performance in fleets of GDI vehicle makes/models in pursuit of this objective.

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DEFINITIONS/ABBREVIATIONS

LTFT	Long Term Fuel Trim
RIFT	Rapid Injector Fouling Test
IPW	Injector Pulse Width
MIL	Malfunction Indicator Lamp
SOT	Start of Test
MOT	Middle of Test
EOT	End of Test
GDI	Gasoline Direct Injection
PFI	Port Fuel Injection
DTBDS	Di-Tert-Butyl Disulfide
TBHP	Tert-Butyl Hydrogen Peroxide
OEM	Original Equipment Manufacturer
SEM	Scanning Electron Microscope
EDX	Energy-Dispersive X-Ray Spectroscopy
BFS	Base Fuel Severity
BFT	Base Fuel Treatability
DCA	Deposit Control Additive

CONTACT INFORMATION

Charles.shanahan@aftonchemical.com

Scott.smith@aftonchemical.com

Brian.sears@aftonchemical.com

APPENDIX

SEM-EDX SPECTRA OF KIA OPTIMA INJECTOR DEPOSITS (FIGURES 1-2)

Kia Optima Injector Deposits on Non-Doped E0 Refinery Gasoline

The non-doped base fuel spectra indicates sulfur still a significant part of the deposit composition.

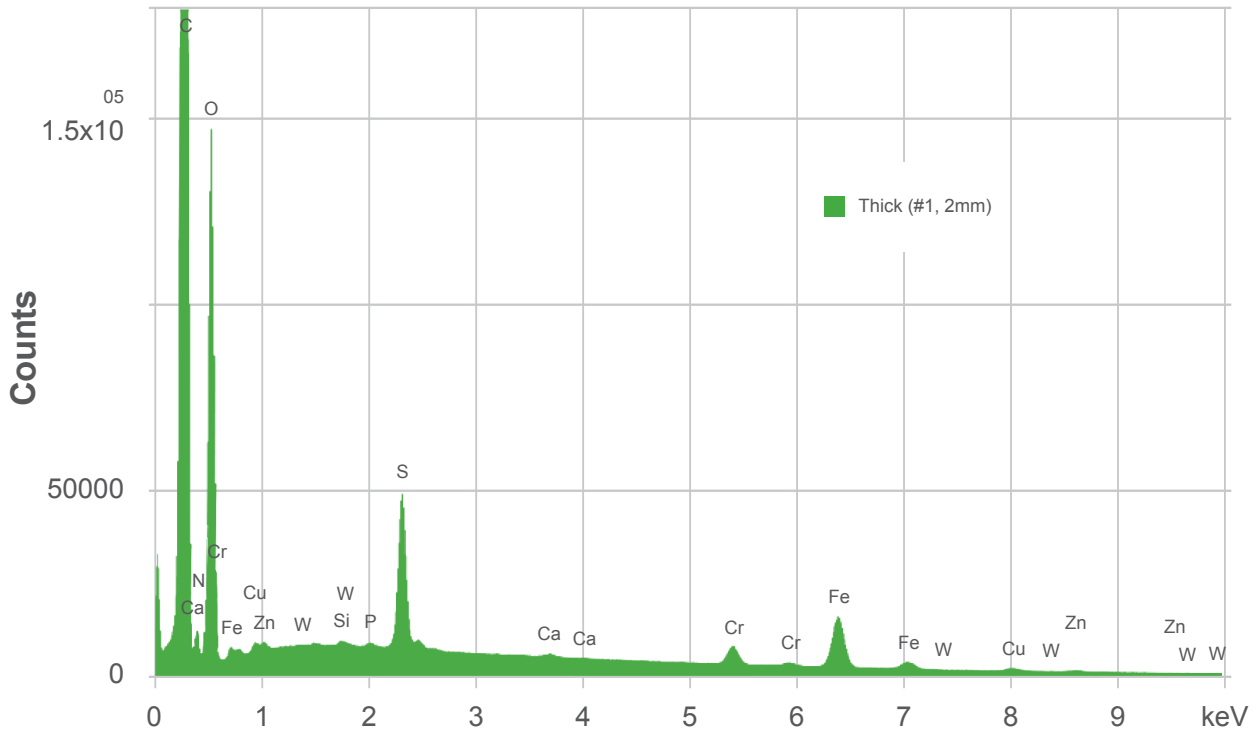


Figure 1.

Kia Optima Injector Deposits on E0 Refinery Gasoline with Chemical Accelerants (DTBDS and TBHP)

The doped base fuel spectra does not contain significantly more sulfur than the undoped base fuel by comparing the EDX spectrum below.

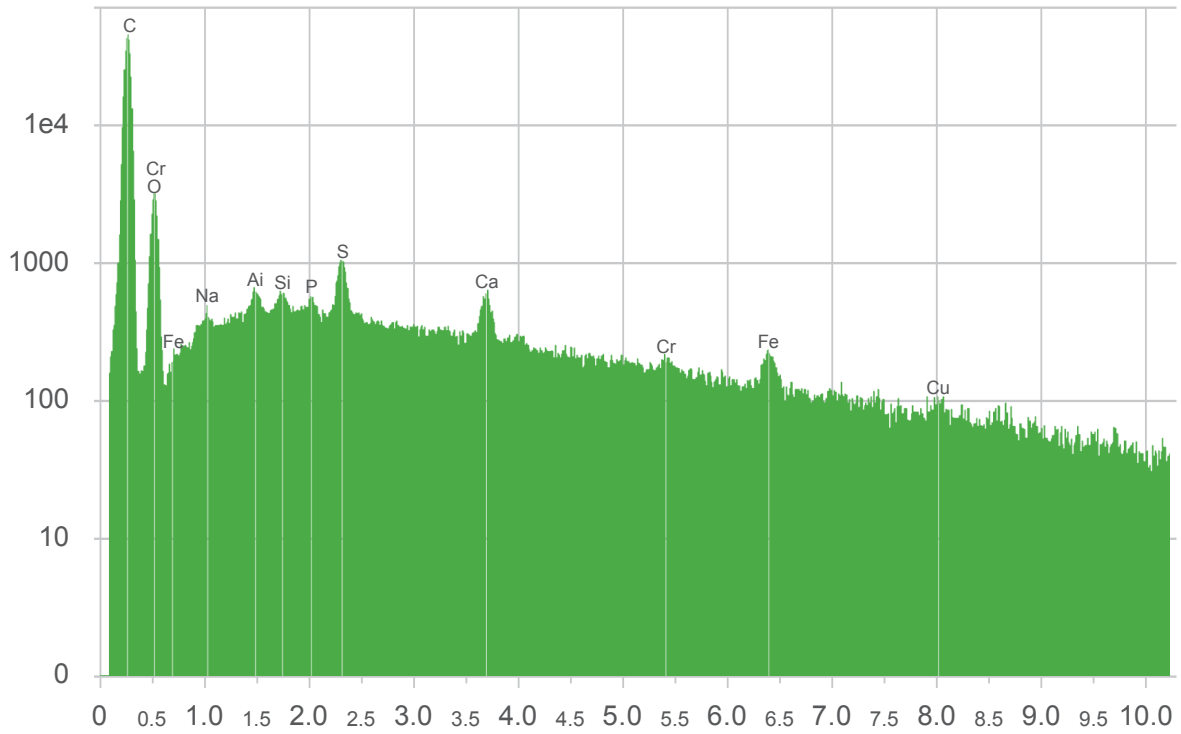


Figure 2.

RF-83-A91 FUEL ANALYSIS (FIGURES 3, 4, 5)

Test	Result	Units	Method	Date	Analyst
API Gravity	55.8	°API	ASTM D-4052	8/2/2016	SB
Benzene in Gasoline	0.22	LV%	ASTM D-3606Q	8/4/2016	LL
Bromine Number	17	g/100g	ASTM D-1159	8/5/2016	LAS
BTU, Gross	19470	BTU/lb	ASTM D-240	8/3/2016	MKM
BTU, Net	18337	BTU/lb	ASTM D-240	8/5/2016	MKM
Detailed Hydrocarbon Analysis					
Capillary Gas Chromatography	See Attached		ASTM D-6733	8/4/2016	MH
Carbon/Hydrogen Content					
Carbon Content	87.53	WT%	ASTM D-5291	8/4/2016	MT
Hydrogen Content	12.42	WT%	ASTM D-5291	8/4/2016	MT

Figure 3.

Test	Result	Units	Method	Date	Analyst
Distillation					
IBP	86.7	Deg F	ASTM D-86Q	8/2/2016	SAK
5% Evap	116.4	Deg F			
10% Evap	132.5	Deg F			
20% Evap	159.5	Deg F			
30% Evap	186.7	Deg F			
40% Evap	208.1	Deg F			
50% Evap	222.0	Deg F			
60% Evap	231.1	Deg F			
70% Evap	241.9	Deg F			
80% Evap	264.8	Deg F			
90% Evap	336.2	Deg F			
95% Evap	354.9	Deg F			
FBP	388.6	Deg F			
Recovery	97.7	Vol %			
Residue	0.9	Vol %			
Loss	1.4	Vol %			
E200	35.8	Vol %			
E300	85.8	Vol %			
Existent Gum Content					
Before Heptane Wash	1.5	mg/100mL	ASTM D-381	8/3/2016	BM
After Heptane Wash	<0.5	mg/100mL	ASTM D-381	8/3/2016	BM
Hydrocarbon Type - FIA					
Aromatics	36.8	LV %	ASTM D-1319Q	8/3/2016	RM
Olefins	10.0	LV %			
Saturates	53.2	LV %			
Induction Period					
Induction Period	960+	min.	ASTM D-525	8/4/2016	BM

Figure 4.

Test	Result	Units	Method	Date	Analyst
Octane					
Research Octane	97.4		ASTM D-2699	8/2/2016	RS
Motor Octane	85.5		ASTM D-2700	8/2/2016	RS
R+M/2	91.4			8/2/2016	RS
Oxygenates in Gasoline					
Methanol	<0.10	LV %	ASTM D-5599Q	8/3/2016	LL
Ethanol	0.10	LV %			
Isopropyl Alcohol	<0.10	LV %			
tert-Butyl Alcohol	<0.10	LV %			
N-Propanol	<0.10	LV %			
Methyl tertiary butyl ether	<0.10	LV %			
sec-Butanol	<0.10	LV %			
Diisopropyl ether	<0.10	LV %			
Isobutanol	<0.10	LV %			
Ethyl tertiary butyl ether	0.10	LV %			
ter-Amyl Alcohol	<0.10	LV %			
N-Butanol	<0.10	LV %			
ter Amyl methyl ether	<0.10	LV %			
Oxygen Content	0.03	WT %			
Potential Gum					
Aging Time	4	Hours	ASTM D-873		
Potential Gum	1.7	mg/100mL	ASTM D-873	8/5/2016	BM
Sulfur Content	170	mg/kg	ASTM D-5453Q	8/3/2016	MT
Vapor Pressure, EPA Equation	8.68	psi @100F	ASTM D-5191Q	8/2/2016	SAK

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Figure 5.

REFINERY E0 GASOLINE WITH ACCELERANTS (DTBDS AND TBHP) FUEL ANALYSIS (FIGURES 6, 7, 8)

Test	Result	Units	Method	Date	Analyst
API Gravity	54.6	°API	ASTM D-4052	8/2/2016	SB
Benzene in Gasoline	0.65	LV %	ASTM D-3606Q	8/4/2016	LL
Bromine Number	23	g/100g	ASTM D-1159	8/5/2016	LAS
BTU, Gross	19546	BTU/lb	ASTM D-240	8/3/2016	MKM
BTU, Net	18376	BTU/lb	ASTM D-240	8/4/2016	MKM
Detailed Hydrocarbon Analysis					
Capillary Gas Chromatography	See Attached		ASTM D-6733	8/4/2016	MH
Carbon/Hydrogen Content					
Carbon Content	87.16	WT %	ASTM D-5291	8/4/2016	MT
Hydrogen Cont	12.83	WT %	ASTM D-5291	8/4/2016	MT

Figure 6.

Test	Result	Units	Method	Date	Analyst
Distillation					
IBP	96.4	Deg F	ASTM D-86Q	8/2/2016	SAK
5% Evap	119.3	Deg F			
10% Evap	131.8	Deg F			
20% Evap	150.3	Deg F			
30% Evap	170.4	Deg F			
40% Evap	195.6	Deg F			
50% Evap	225.4	Deg F			
60% Evap	253.6	Deg F			
70% Evap	279.2	Deg F			
80% Evap	308.0	Deg F			
90% Evap	343.6	Deg F			
95% Evap	370.2	Deg F			
FBP	420.9	Deg F			
Recovery	97.2	Vol %			
Residue	1.1	Vol %			
Loss	1.7	Vol %			
E200	41.6	Vol %			
E300	77.4	Vol %			
Existent Gum Content					
Before Heptane Wash	8.0	mg/100mL	ASTM D-381	8/3/2016	BM
After Heptane Wash	2.0	mg/100mL	ASTM D-381	8/3/2016	BM
Hydrocarbon Type - FIA					
Aromatics	37.6	LV %	ASTM D-1319Q	8/3/2016	RM
Olefins	12.0	LV %			
Saturates	50.4	LV %			
Induction Period	960+	min.	ASTM D-525	8/5/2016	BM

Figure 7.

Test	Result	Units	Method	Date	Analyst
Octane					
Research Octane	91.2		ASTM D-2699	8/2/2016	RS
Motor Octane	80.7		ASTM D-2700	8/2/2016	RS
R+M/2	86.0			8/2/2016	RS
Oxygenates in Gasoline					
Methanol	<0.10	LV %	ASTM D-5599Q	8/3/2016	LL
Ethanol	<0.10	LV %			
Isopropyl Alcohol	<0.10	LV %			
tert-Butyl Alcohol	<0.10	LV %			
N-Propanol	<0.10	LV %			
Methyl tertiary butyl ether	<0.10	LV %			
sec-Butanol	<0.10	LV %			
Diisopropyl ether	<0.10	LV %			
Isobutanol	<0.10	LV %			
Ethyl tertiary butyl ether	<0.10	LV %			
ter-Amyl Alcohol	<0.10	LV %			
N-Butanol	<0.10	LV %			
ter Amyl methyl ether	<0.10	LV %			
Oxygen Content	<0.02	WT %			
Potential Gum					
Aging Time	4	Hours	ASTM D-873	8/4/2016	SAK
Potential Gum	8.6	mg/100mL	ASTM D-873	8/9/2016	SAK
Sulfur Content	170	mg/kg	ASTM D-5453Q	8/3/2016	MT
Vapor Pressure, EPA Equation	7.71	psi @100F	ASTM D-5191Q	8/2/2016	BM

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Figure 8.

ASIA PACIFIC

Afton Chemical Asia Pte. Ltd.
111 Somerset Road #09-05
TripleOne Somerset
Singapore
238164
T: +65 6732-0822

LATIN AMERICA

Afton Chemical Industria de Aditivos Ltda.
Estrada da Boa Esperança, 650 Parte
Bom Pastor - Belford Roxo – RJ
26.110-120
Brazil
T: +55 21 3559-7576

EMEA

Afton Chemical Limited
London Road, Bracknell
Berkshire
RG12 2UW
England
T: +44 0 1344 304-141

NORTH AMERICA

Afton Chemical Corporation
500 Spring Street
Richmond
VA 23219
U.S.A.
T: +1 804 788-5800