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FUEL ADDITIVES AND THEIR APPLICATION IN ENGINES USING BIOFUELS

Abstract

During the last two decades great strides have been taken by the European parliament, in consultation with oil companies and car manufacturers, to improve air quality within the European union. Air quality improvements have mostly been achieved by the publication of vehicle emissions directives forcing car manufacturers to design more efficient vehicle technology. These vehicles can only operate to their design specification when appropriate quality fuels are available and this has led to publication of the fuels quality directives and the implementation of stringent diesel and gasoline fuel specifications.

In addition fuel producers and retailers have the added challenge of the biofuels directive leading to the need to incorporate FAME and ethanol into commercial diesel fuel and commercial gasoline respectively. There has been a stepwise increase in biofuel use in Europe driven by the bio-fuels directive 2009/28/EC on the promotion of the use of energy from renewable sources. The share of energy from renewable resources is planned to rise to a minimum 20% in every member state by 2020 with a 10% renewable contribution to transportation energy consumption. The introduction of biofuels together with modern direct injection engine technology has led to a number of concerns related to efficient vehicle operation. These modern engines are very sensitive to deposits and bio-fuels are known to have a greater propensity to produce deposits than fossil fuel.

As a consequence, in cooperation with automobile manufacturers and industry bodies investigations are performed in order to ensure that biofuels are fit for purpose and allow vehicles to operate to their design specification. In this paper we will discuss the methodologies used in these investigations and data generated which highlights the benefits of using gasoline and diesel performance additives in modern vehicles operating on today's fuel quality.

Key words: *gasoline, diesel, biofules, deposits, performance additives*

ADITIVI ZA GORIVA I NJIHOVA PRIMJENA NA MOTORE KOJI KORISTE BIOGORIVA

Sažetak

Tijekom posljednja dva desetljeća Europski parlament je poduzeo velike korake u dogovoru s naftnim tvrtkama i proizvođačima automobila, kako bi se poboljšala kvaliteta zraka u Europskoj uniji. Poboljšanja kvalitete zraka uglavnom su postignuta objavljivanjem uredbi o emisijama vozila prisiljavajući proizvođače automobila da projektiraju vozila pomoću učinkovitije tehnologije. Ova vozila mogu raditi samo uz zadovoljenje propisanih specifikacija kada su dostupna goriva zadovoljavajuće kvalitete što je dovelo do objavljivanja uredbi o kvaliteti goriva i do primjene strogih specifikacija o dizelskim i benzinskim gorivima. Osim toga, proizvođači i trgovci gorivima imaju dodani izazov definiran direktivom o biogorivima koja govori o potrebi dodavanja FAME i etanola u komercijalna dizelska goriva i benzine. Tako dolazi do postupnog povećanja potrošnje biogoriva u Europi što je uzrokovala uredba o biogorivima 2009/28/EC koja promiče korištenje energije iz obnovljivih izvora. Planira se porast udjela obnovljivih izvora na minimalno 10 % u svakoj pojedinoj državi članici do 2020. Uvođenje biogoriva zajedno s modernim motorima s izravnim ubrizgavanjem uzrokovalo je brojne brige vezane za učinkovit rad vozila. Moderni motori su vrlo osjetljivi na stvaranje taloga, a za biogoriva se zna da imaju veću sklonost stvaranju taloga u usporedbi s fosilnim gorivima.

Zbog toga se u suradnji s proizvođačima automobila i industrijom provode istraživanja kako bi se osiguralo da biogoriva odgovore na postavljene zahtjeve i omoguće rad vozila u skladu s projektiranim specifikacijama. U ovom se radu raspravlja metodologija korištena u tim istraživanjima kao i dobiveni podaci koji naglašavaju prednosti korištenja aditiva za benzinska i dizelska goriva za vozila koja rade uz današnju kvalitetu goriva.

Ključne riječi: *benzin, dizel, biogoriva, talozi, aditivi*

1. Introduction

As part of the Kyoto Agreement, the European Union committed to reducing its emissions of CO_2 by 8 percent by between 2008 and 2012. The life cycle analysis (LCA) approach to the overall atmospheric CO_2 contribution of a fuel suggests that bio-fuels produce about 50 percent less CO_2 than mineral fuels. This has provided the main incentive in persuading individual governments, and now the European Commission, to support the development of the bio-fuels market as an important contribution to meeting their overall emission targets.

In 2003, Directives 2003/30/EC and 2003/96/EC were formally adopted by the European Parliament. The former Directive set indicative targets for consumption of biofuels, and other renewable fuels, with a reference value of 2 percent of the total energy content of the transport fuels markets in each member state by December 2005. This was not obligatory however, and many countries lagged behind on this quota. Further targets were then set and by 2010 the EU hoped that biofuels would

account for 5.75 percent of all transport fuels. Directive 2003/96/EC allowed member states to exempt biofuels from the normal excise duties applied to transport fuels.
This was considered to be crucial to the success of the biodiesel market in particular, which is reliant on tax advantages to compete with mineral diesel at the pumps. The market has thrived in those countries where either adequate tax exemptions or punitive taxation for non-compliance were put in place, whilst there was very little activity in other countries. Directive 2009/28/EC repealed Directive 2003/30/EC, and required that 10% of energy used in transport should come from renewable sources by 2020. To support this, the Fuel Quality Directive, 2009/30/EC, extended the permitted content of ethanol in gasoline to 10%, whilst confirming the use of up to 7% biodiesel blends. The European specifications for diesel (EN590) and gasoline (EN228) are being modified accordingly.

2. Concerns related to bio-diesel

Freshly produced vegetable oils are protected from oxidation by the presence of naturally occurring antioxidants. The manufacturing process for biodiesel removes natural antioxidants, leaving the fuel unprotected from oxidative degradation. Oxidation of biodiesel by contact with air and metal surfaces results in the formation of hydro-peroxides. These induce free-radical chain reactions that lead to decomposition into low molecular weight, highly oxidized species (aldehydes, ketones, acids etc) and high-molecular-weight polymeric materials (gums). These gums cause poor combustion and other engine problems such as deposits on injectors and pistons. The presence of high-molecular weight insoluble gums can also lead to fuel-filter plugging.

The European specification for Bio-fuel (FAME), EN 14214, has been designed to control the critical parameters to ensure that the addition of FAME to fossil fuel will produce fuels both meeting the European fuel specifications but, more importantly, also being fit for purpose. The oxidative stability concerns are addressed by introduction of a minimum induction period of 6 hours (soon to be extended to 8 hours) measured by the Rancimat test. This generally requires the addition of antioxidants to the FAME during manufacture. However, car manufacturers still have concerns related to ‘‘Fit for purpose’’ and the main problems are injector deposits which can have a serious impact on engine and vehicle performance.

2.1. Injector deposits

All diesel fuels have a tendency to form small amounts of hard, carbonaceous deposits on the fuel injector nozzles of both direct injection and indirect injection diesel engines. In the case of indirect injection, the engines were optimized for performance with a limited amount of injector deposit present. In both types of engine, the buildup of excessive amounts of these deposits will disrupt the spray pattern of the fuel from the nozzle (Figure 1), which can lead to serious drivability problems. Increased fuel consumption, high noise levels and increased emissions are some of the other problems attributed to excessive nozzle coking.

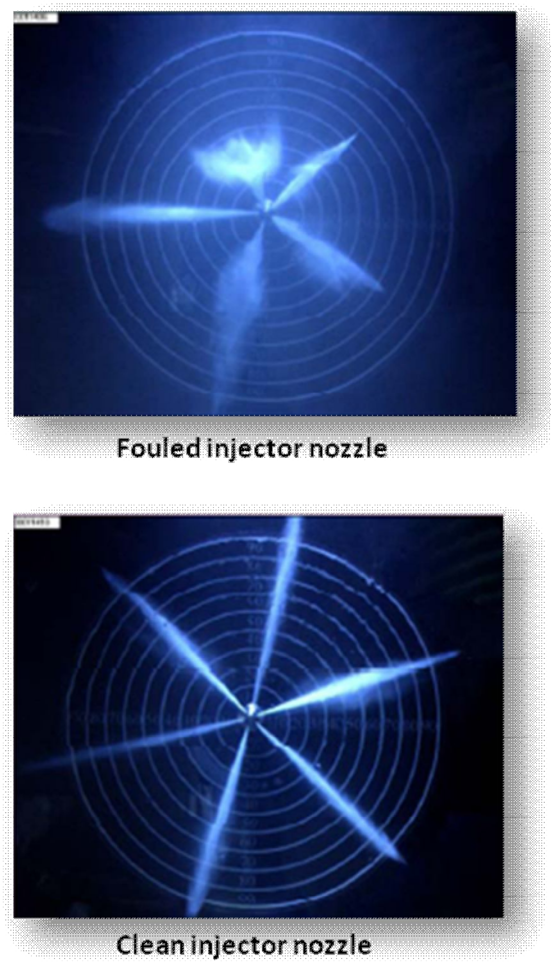


Figure 1: Illustration of importance of fuel injection system cleanliness

There are two basic engine designs for diesel passenger cars in the current European car parc. Older designs of passenger diesel engines are based upon indirect injection technology where the fuel is sprayed through a pintle injector into a pre-combustion chamber. The industry standard engine test for indirect injection passenger technology is based upon the Peugeot XUD-9 engine. This test procedure was first developed in the mid 1980's by a working group affiliated to the CEC. The initial test was published as the CEC-F-23-X-95 and this test was under development for up to 10 years.

The graph below (Figure 2) indicates the amount of flow loss that occurs in this standard engine test with 100% fossil fuels and the impact that adding 10% FAME has on injector flow loss. Flow loss is caused by deposit build up on the injectors (see Fig. 1). This data shows that the presence of FAME has only a slight impact on deposit build up in this engine technology. The data also shows that diesel detergent additives are fully capable of delivering the required level of deposit control.

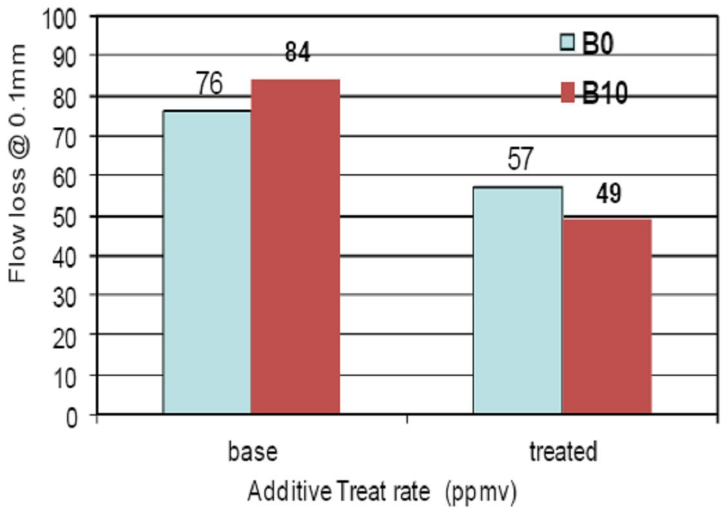


Figure 1: Impact of FAME on injector fouling
(coking deposits: Peugeot XUD-9 Industry Engine Test - impact of biodiesel)

The pintle injectors used in the XUD-9 test were designed to deliver optimal performance with a defined level of coking, in the range 25-50% maximum flow loss, as demonstrated in the paper SAE 912328 by Reading et al. This test has shown that the use of Afton chemicals latest detergent technology will ensure this level of performance is maintained in the presence of FAME.

More recently, direct injection common rail engines have been introduced to the European market by major car manufacturers as a means to meet the stringent emission limits of current European legislation. These modern diesel engines are fitted with very precise injection technology designed to help deliver better combustion efficiency with a consequent reduction in tailpipe emissions. However, over time deposits will build up on the critical parts of the diesel fuel injection equipment and these will not allow the engine to operate to its design specification. To maintain the performance levels attributed to modern engine designs it is important to keep the injectors clean and free of deposits.

As a consequence, the current industry standard coking test, CEC F-23-01 (XUD-9) mentioned above no longer meets the needs of the modern diesel car parc. A new test has recently been developed to monitor the performance of fuels to ensure that modern diesel engines are protected against the power loss and spray pattern degradation that can result from deposit build up on injectors. The new test is based upon the Peugeot DW10 2.0 litre HDi engine operated with multi hole 'sensitive' injectors indicative of EURO V applications and supplied by Siemens. Engine power loss is evaluated during a 72 hour test cycle which consists of a total running time of 32 hours. Vehicle manufacturers are indicating that 2% power loss could be considered as an acceptable performance limit for this test. The test now has official status and has been allocated the CEC F-98-08 (DW-10) nomenclature.

Testing conducted in this engine test has shown that the addition of 10% FAME to fossil fuels leads to excessive injector deposit formation which manifests itself in power loss. Testing has been conducted in the European reference fuel blended with 10% FAME and the impact on power loss can be readily seen. The graph in Figure 3 demonstrates how diesel fuel loses power in the presence of FAME and how, through the use of the latest detergent technology, this power loss can be controlled.

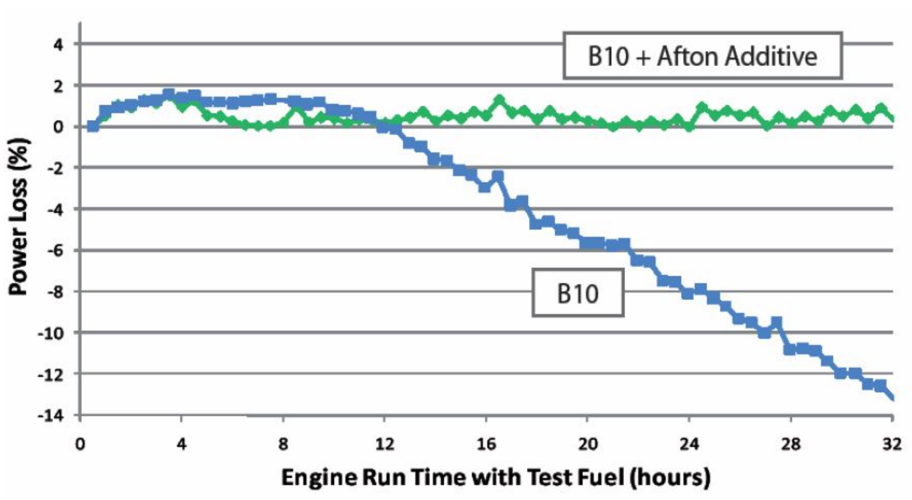


Figure 3: Power loss in dependence on engine run time with test fuel B10 with and without additive
(coking deposits: DW10 Industry Engine Test - impact of biodiesel)

2.2. Internal injector deposits

Reports of problems with high pressure common rail diesel (HPCR) engines started in 2008. The problems were related to poor driveability, rough running and starting problems at low temperatures. These problems seemed to coincide with the introduction of low sulphur diesel fuel and the latest HPCR technology. As the leading supplier of diesel performance additives, Afton chemical was asked to investigate this problem in order to gain a better understanding of the root cause and try to offer a potential solution. The approach adopted by the Afton research team was analyses of the deposits found on the injectors of problem vehicles in the field in order to get an indication of the mechanism leading to deposit formation. This analysis showed that the deposits were mostly insoluble sodium carboxylate salts. One potential source of these deposits was from the manufacturing process for Bio-fuel. The diagram in Figure 4 gives an indication as to the potential source of the problem.

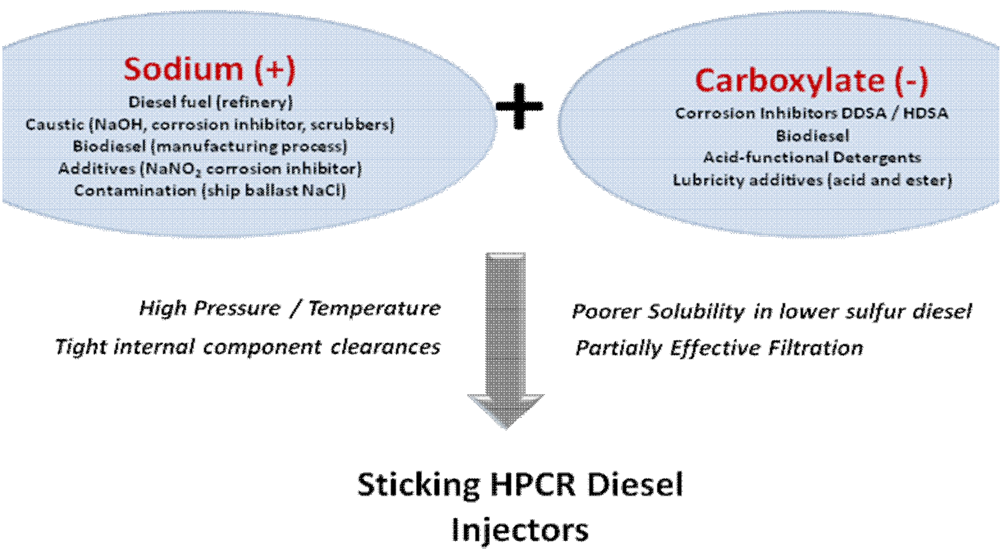


Figure 4: Mechanism of carboxylate internal deposit formation

The next logical step in the investigation was to try to reproduce the same type of deposits in a controlled engine test so that possible solutions could be evaluated. Afton engineers developed an engine test based upon the DW-10 engine and by the addition of representative amounts of sodium and DDS acid were able to produce deposits which were chemically very similar to the deposits seen in returned injectors from the field as can be seen in Figure 5.

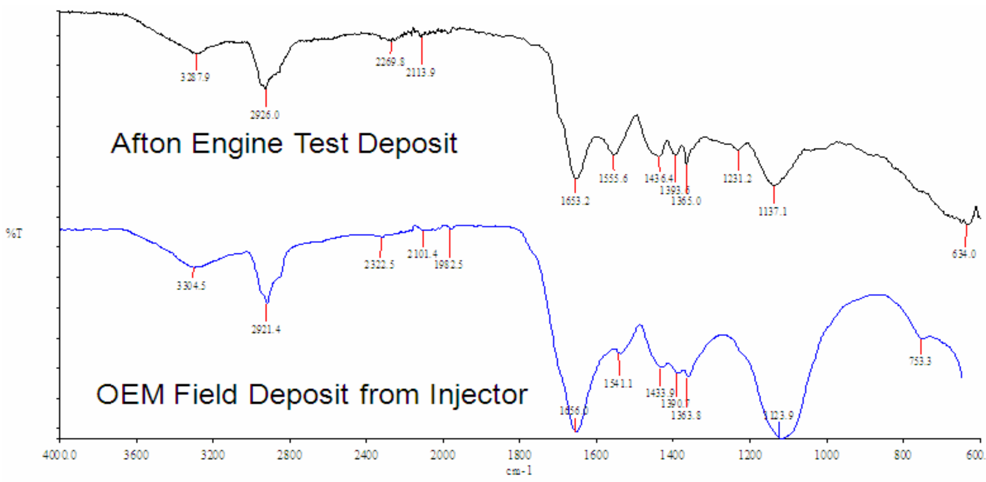


Figure 5: IR spectra of engine test deposit and OEM field deposit from injector

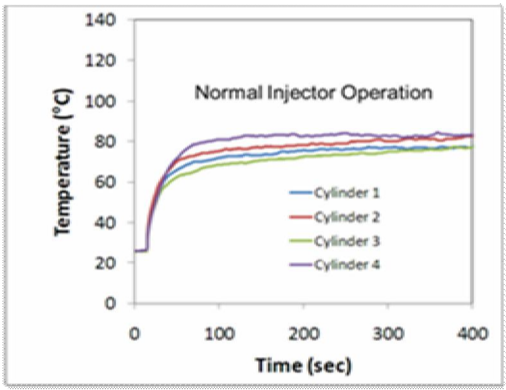
Engine testing clearly showed that the use of the latest diesel detergent additive technology would not only prevent the formation of internal deposits but also remove existing deposits leading to enhanced engine performance. An example of this performance is illustrated in Figure 6. In this engine test any increase in exhaust temperature is a clear indication of injector sticking. The graph on the left indicates no sticking at the start of the test but after 6hours operation on the base fuel there are clear signs of two injectors having sufficient deposits to cause sticking leading to an increase in exhaust temperature. Switching to the same fuel treated with Greenclean™ additive technology has removed deposits leading to restoration of normal engine operation.

3. Concerns related to bio-gasoline

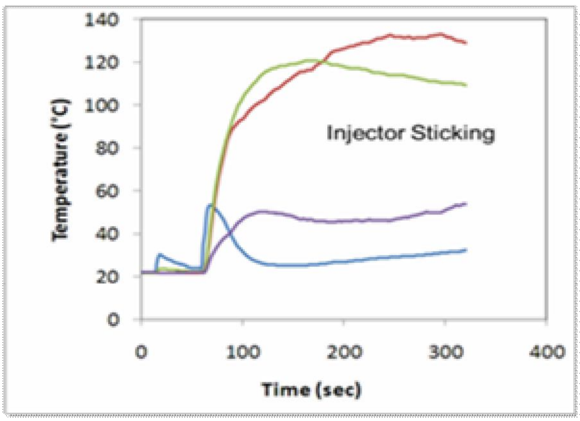
In addition to promoting bio-diesel the European community has recognised the need to introduce Bio-gasoline. This started with the introduction of 5% ethanol (E5) but more recently the EN 228 specification has been amended to allow the use of 10% ethanol (E10) together with a protection grade for older vehicles which is the 98 octane gasoline blended with 5% ethanol.

As with bio-diesel the main concern related to the blending of ethanol with gasoline is the impact of deposits on the performance of the engine. In the older port fuel injection gasoline engines this concern would be related to the deposit build up on inlet valves that can lead to serious driveability problems. More recently, with the introduction of direct injection engine technology the focus is shifting to deposit build up on injectors.

(a)



(b)



(c)

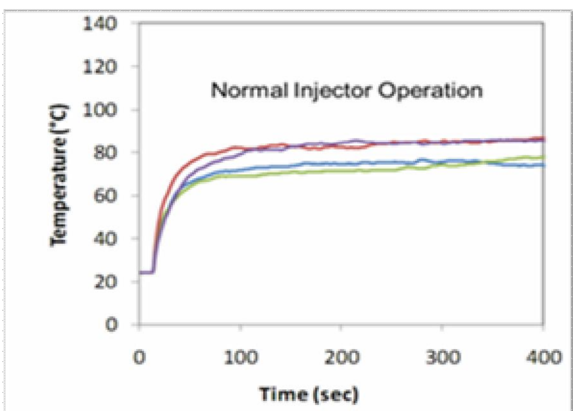


Figure 6: Cylinder exhaust temperatures on cold start: (a) start-of-test, (b) after 6 h, no additive, (c) after 16 h with additive (all fuels contained sodium ion and DDS acid)

In addition to deposit control there are concerns related to corrosion since ethanol has a high affinity for water which will lead to increased corrosion both during storage and during engine operation.

3.1. Inlet valve deposits

The impact of inlet valve deposits on gasoline engine driveability has been recognised for a number of years and it is now common practice for gasoline marketers to use an effective detergent package. The introduction of 10% ethanol has raised question related to the impact on deposits in the base fuel together with the need for reassurance that current gasoline detergents are capable of reducing deposits to the level required for optimal engine performance.

The graph shown in Figure 7 gives an indication of the propensity for E10 gasoline to produce inlet valve deposits. This testing was conducted in the European standard inlet valve engine test using the Mercedes M102E (CEC-F-05). The data indicates significant differences depending on fuel severity and also indicates that the addition of ethanol at the level of 10% does not significantly change the severity versus 100% fossil fuel.

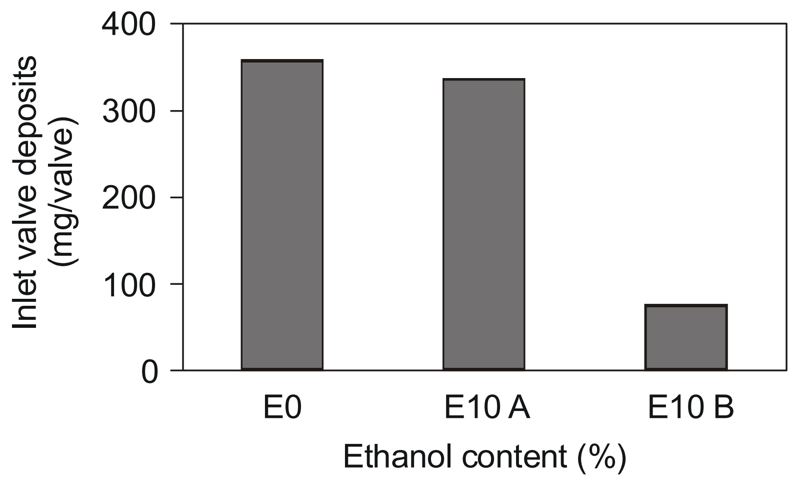


Figure 7: Impact of ethanol on inlet valve deposits (mg/valve)

Further testing has been conducted to validate the performance of latest gasoline detergent technology in ethanol containing gasoline. Once again testing has been conducted using the Mercedes M102E engine test and the ethanol used meets the European quality specification for ethanol. The excellent “Keep clean” performance of Afton chemical’s latest gasoline additive technology in E10 gasoline is shown in Figure 8.

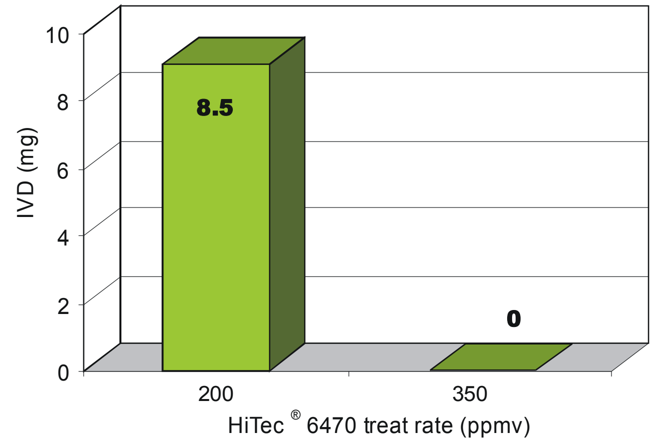


Figure 8: Deposit control in gasoline / ethanol (10 %) blends

We have also seen the introduction of ''Flexi vehicles'' which are designed to operate on fuels containing up to 85% ethanol. These vehicles have a sensor in the fuel tank which detects the level of alcohol in the fuel and then adjusts the engine operation accordingly. Engine testing has shown that these vehicles still have the propensity to create inlet valve deposits when operating on E85 gasoline and hence require the use of a deposit control additive. Testing has shown that conventional gasoline deposit control additives are not suitable for use in E85 gasoline due to the lack of additive solubility in fuels containing such a high level of ethanol. Afton Chemical has developed very effective deposit control additives that can be used in E85 gasoline. The ability of this additive to control deposits in this type of vehicle is shown in Figure 9.

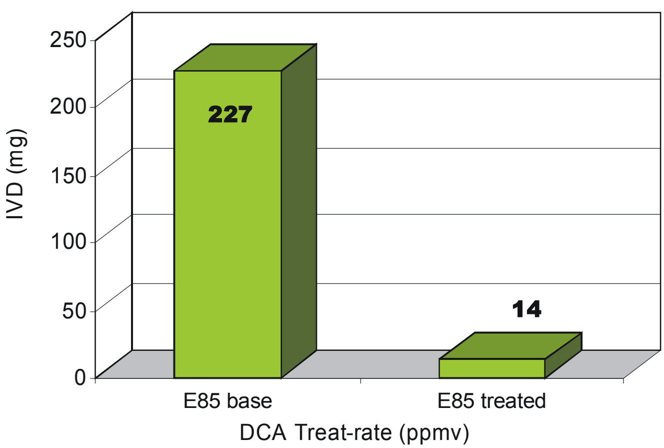


Figure 9: Deposit control in gasoline / ethanol (15 %) blends

3.2. Corrosion protection

Ethanol has an affinity for watering and this has led to concerns related to water entrapment leading to excessive corrosion during the storage of bio-gasoline and during transportation. The corrosion problem can be addressed by the addition of a corrosion inhibitor to the ethanol during manufacture. The first corrosion inhibitors identified for ethanol treatment were found to contribute to gasoline engine deposits. Since then additive industry has developed corrosion inhibitors which are not only very effective in reducing corrosion but are also neutral in terms of gasoline engine deposits. This corrosion inhibitor is commercially available under the BioTec brand The performance of the corrosion inhibitor is shown in Figure 10.


(a)


(b)

Figure 10: Corrosion protection in ethanol blends:
(a) gasoline + 10% ethanol + 30 ppm BioTEC™ 9880 inhibitor, 0% rust, A-rating;
(b) base gasoline, 100% rust, E-rating;

Conclusions

This study has clearly demonstrated that the use of bio fuels such as fatty acid methyl esters (FAME) in diesel and ethanol in gasoline introduces new challenges to the industry in terms of ensuring fuels are fit for purpose. Once again the additive industry has been called upon to not only demonstrate that conventional additives are compatible with bio-fuels but also to develop new additive technology in order to cost effectively address new performance concerns related to the use of these environmentally friendly fuels. There have been a number on instances of diesel injector sticking both in Europe and North America and this has often been associated with the inclusion of FAME in diesel. The data shown in this paper is clear evidence that additive industry latest diesel deposit control additive technology is capable of controlling injector sticking. Early on during the inclusion of ethanol into gasoline concerns were raised in terms of excessive corrosion but the additive industry was able to offer a solution which is now fully accepted within the industry.

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