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EXPERIENCE WITH BIO-ETHANOL GASOLINE BLENDS

Abstract

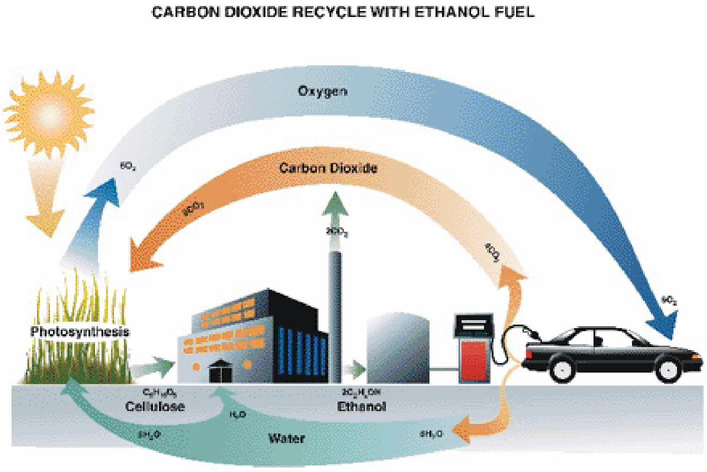
Ethanol, especially from biogenic sources, is increasingly being used as a component in transportation fuels in many regions of the world. Widespread use may lead to problems for manufacturers of the fuels, for the supply chain, for the fuel marketers and, last but not least, for the automobile user. These difficulties include corrosion due to water uptake and more engine deposits as a result of impurities in the ethanol. Each partner in the industry faces the challenge of minimizing the risk in his segment while taking maximum benefit from the use of ethanol.

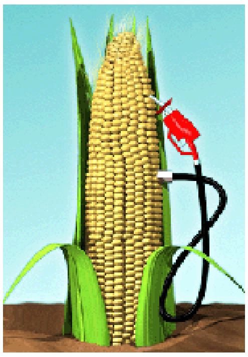
The development is viewed as an opportunity to further improve the quality of fuels regarding fuel economy, emissions control and driveability. On the basis of results obtained in engine tests, laboratory tests and the application of our additives in ethanol fuels in the US, Brazil, Thailand, China, Sweden and other markets, the presentation shows that modern synthetic performance additives are top-performing in most ethanol fuels around the world. The fuels available in certain markets may require an increase in the overall additive dosage or in the level of corrosion inhibitor. A special problem with increased valve-sticking tendency in Scandinavia required the development of a new additive package.

Introduction

The idea behind bio-ethanol for gasoline is very well known: sun power grows sugar-containing plants, such as sugar cane or corn. Fermentation and several process steps produce bio-ethanol, which is than blended with gasoline (Figure 1).

Figure 1: Carbon dioxide recycling with ethanol fuel (Source CANEMET Technology Centre –Ottawa)





Of cause it is not such easy as shown in this cartoon. You need a lot of know-how to produce high quality gasoline and it's even more difficult to guarantee this quality when ethanol is used.

Global issue

Bio-ethanol is a global issue; almost all countries are either using ethanol or are in discussion to use bio-ethanol in the near future (Figure 2).

However, the motivation to use renewable fuel varies from country to country. Some governments push bio-fuels to fulfil Kyoto protocol requirements. Use of bio-fuels reduces dependence on crude oil imports and can help to develop agriculture and rural areas in such countries.

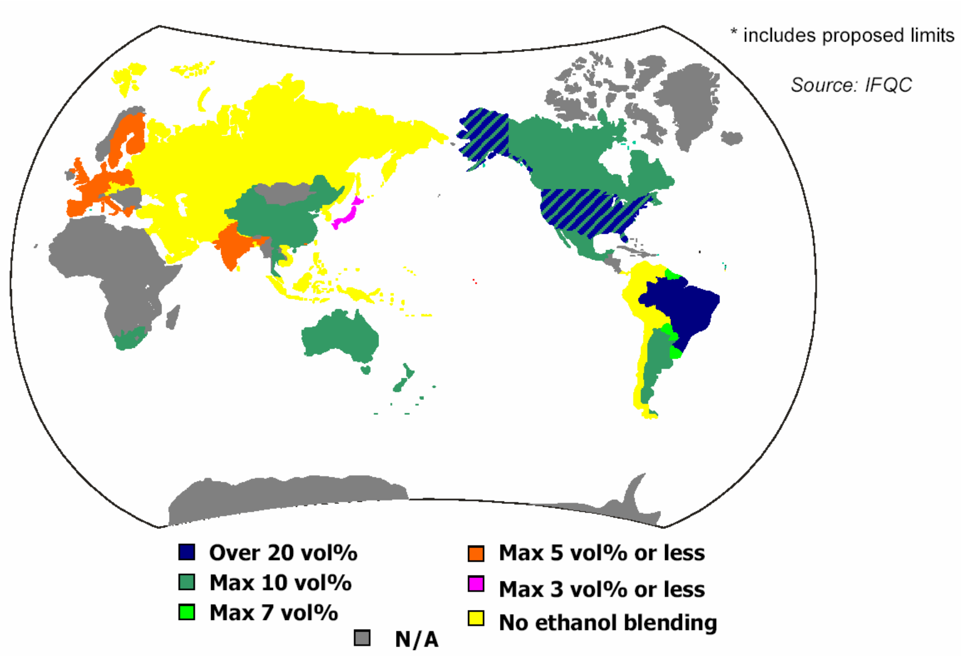
Quality requirements

Bio-ethanol is produced by fermentation of e.g. sugar cane and corn. Water and other critical by-products such as acids and sulphates can cause multiple problems. The ASTM D4806 is just an example for an important specification of fuel grade ethanol. The mentioned parameters shall guarantee a high quality standard of the ethanol (Table 1).

Table 1: Fuel Grade Ethanol Specification

Property	USA ASTM D 4806-04a Specification	ASTM Test Method
Ethanol, vol%, min	92,1	ASTM D 5501
Solvent-washed gum content, max, mg/100ml	5	ASTM D 381
Water content, vol%, max	1	ASTM E 203
Denaturant content Vol%, min Vol% max	 1,96 4,76	
Inorganic chloride content Mass ppm (mg/L), max	 40 (32)	ASTM D 512
Copper, max, ppm	0,1	ASTM D 1688
Acetic Acid, max, g/L	0,056	
pHe	6,5-9,0	ASTM D 6423
Sulfur, max. mg/kg	30	ASTM D 2622, 3120, 5453, 6428

Figure 2: Legal blending limits of Ethanol in 2005 (Presented at SAE Fuels & Lubes Meeting, May 13. 2005 – Source: IFQC)



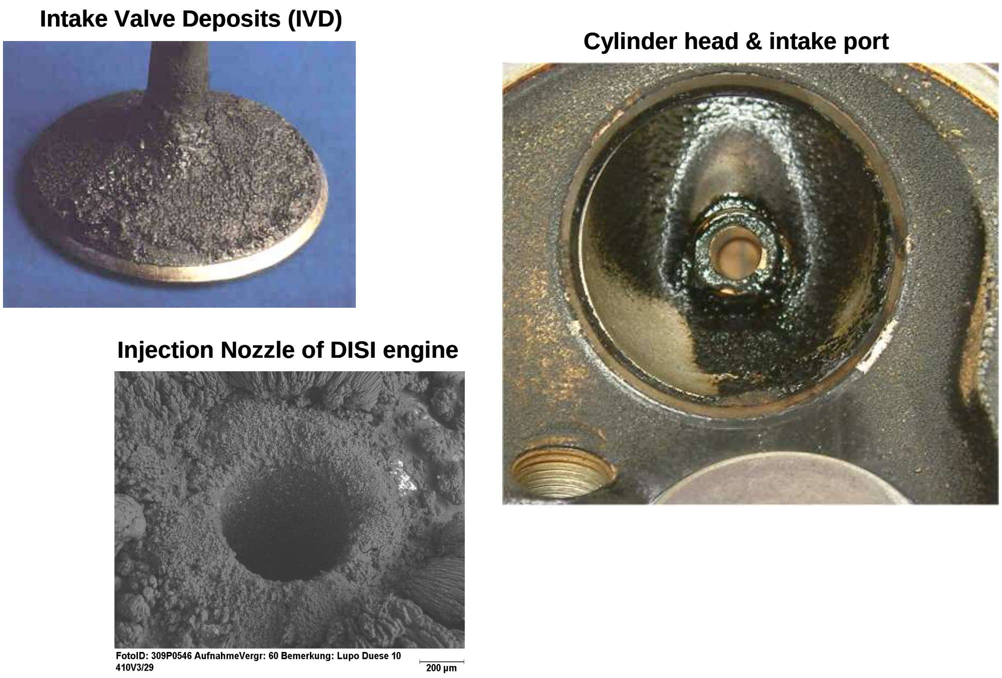
However, it is questionable if these parameters are sufficient to avoid fuel related problems.

Other specifications such as the Polish, Ukrainian and Swedish specifications are much more stringent but other countries do not even have a standard.

Quality improvement

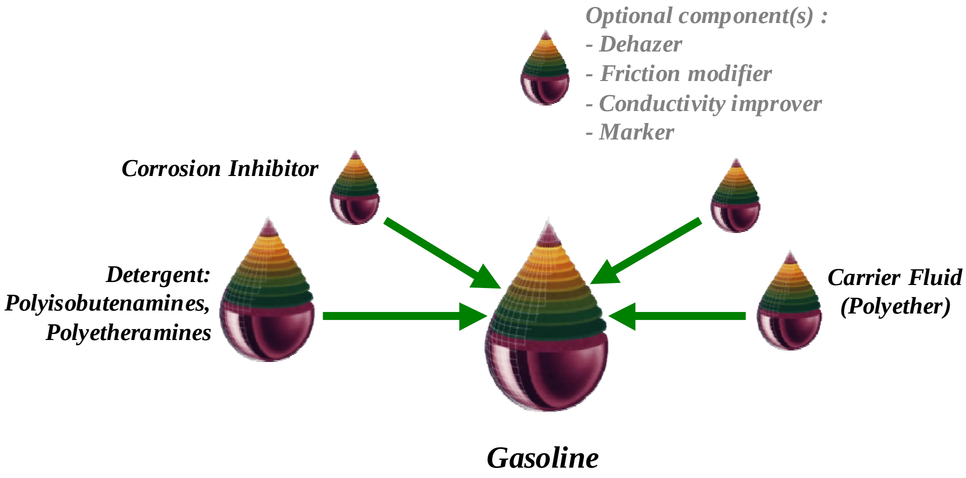
It is well known that spark ignited combustion engines can build up severe deposits in conventional port fuel injection engines as well as in gasoline direct injected engines. These deposits increase fuel consumption and cause higher exhaust emissions. They furthermore cause poor performance in drivability and reduce the average lifetime of gasoline engines (Figure 3).

Figure 3: Critical Deposits in PFI and DISI Engines



Therefore car manufactures recommend using gasoline additives in the World Wide Fuel Charter (WWFC) to improve the quality of gasoline. There are multiple gasoline additive technologies present in the market. However, modern gasoline performance additives (GPA) should contain a significant amount of a detergent mostly in combination with synthetic carrier fluids. Corrosion inhibitors are also a must as well as solvents to reach certain viscosity requirements (Figure 4).

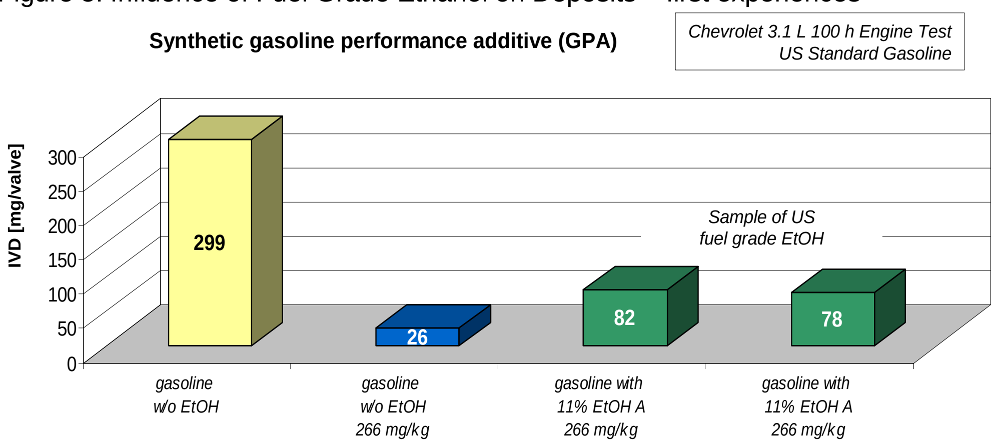
Figure 4: Gasoline Performance Additive



Test experiences

We start the presentation of our data with some old results from the US where bio-ethanol has been introduced in the early 90ies. A 100h test with a Chevrolet 3.1 L engine showed differences between gasoline without and gasoline with fuel grade ethanol. The test evaluates intake valve deposits (IVD) and relates to the cleanliness of the intake system of a PFI engine (Figure 5).

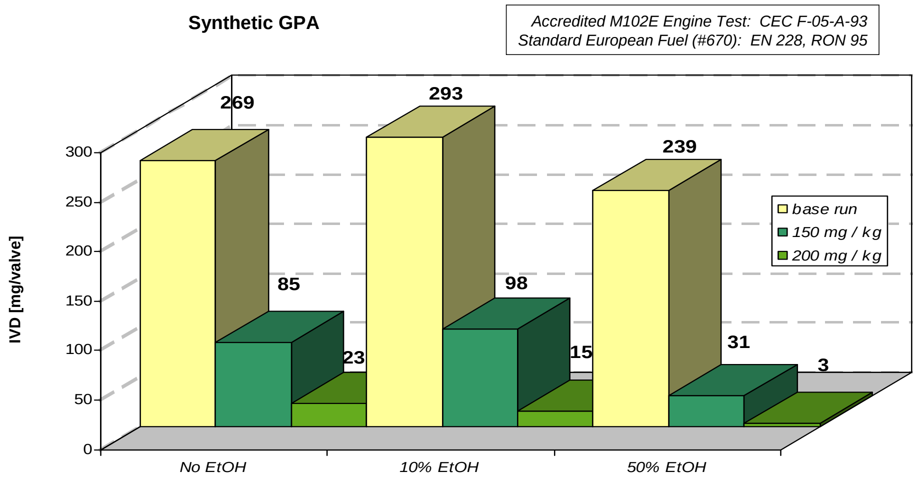
Figure 5: Influence of Fuel Grade Ethanol on Deposits – first experiences



The base gasoline without ethanol caused 299 mg IVD per valve. The use of only 266 mg/kg of a synthetic GPA clearly helped to avoid the formation of deposits almost perfectly. However, when 11 Vol% of a fuel grade ethanol was present in the additized gasoline the benefit was less significant. In particular we found approximately 80 mg IVD instead of 26 mg IVD - so deposits increased significantly by an US fuel grade ethanol.

It was worthwhile to evaluate whether the chemical component ethanol causes this debit or if this is the effect of some fuel grade ethanol qualities only. We therefore performed a CEC F05-A-93 IVD test series in a Mercedes M102E 2.3L engine with blends of an European RON95 gasoline and a chemical grade (99.9%) ethanol (Figure 6).

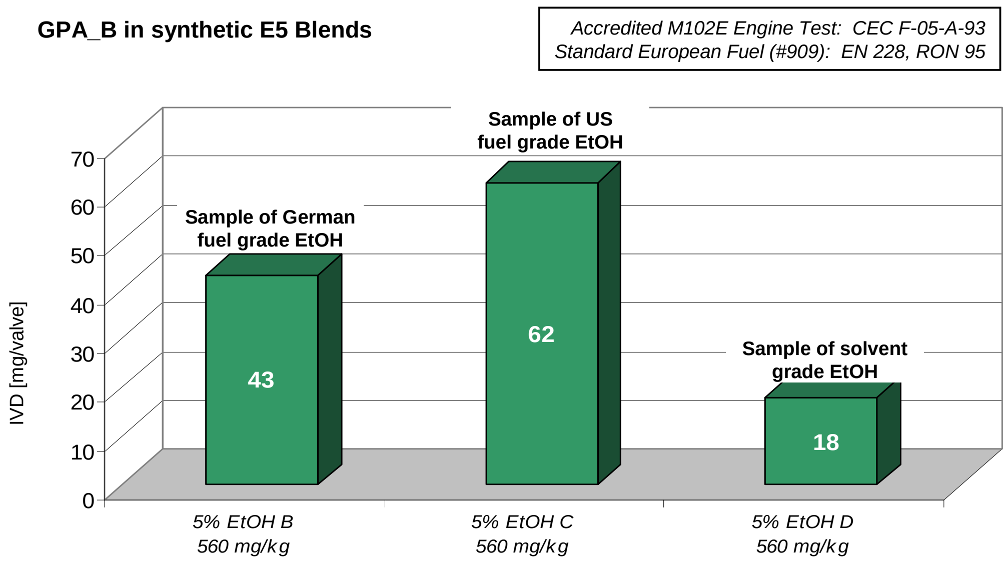
Figure 6: Influence of clean Ethanol on Deposits



The series of non-additized runs showed no negative impact of ethanol; contra wise IVD decreased when 50 Vol% of bio-ethanol had been used. This tendency has been confirmed when we tested the same blends with 150 mg/kg and 200 mg/kg GPA respectively. At low concentrations clean ethanol has no impact on IVD. Ethanol rich blends can even reduce deposits.

Very recently we tested three different types of ethanol in blends of European RON 95 gasoline with 5 Vol% of ethanol (Figure 7).

Figure 7: Influence of Fuel Grade Ethanol on Deposits – results in E5 gasoline



Since we used the same GPA and the same treat rates in all cases, the differences in IVD must be caused by the different ethanol qualities. One therefore can also expect that different commercial fuel grade ethanol qualities will result in different IVD levels.

We can summarize that some fuel grade ethanol qualities can increase deposits so that mineral oil companies may have to increase detergent levels. However, a robust treat level of a good GPA should even cover the differences caused by fuel grade ethanol.

We now address an issue which is usually not in the focus of mineral oil companies but should be seriously evaluated by the additive suppliers. The CEC F-16-T-96 test is a no-harm test which proves that the additive does not cause valve sticking. One test cycle includes to operate the engine for 2.5 h with the test gasoline and cool down the engine to +5℃ over night. Next morning th e electrical starter moves the engine. In case the valves open and close smoothly you will see full compression in all four cylinders. Passing this cycle three times without any stuck valve the test has been passed successfully. For some regions it is worthwhile to run this test at lower temperatures, even if this is not according to the CEC procedure. Scandinavia for example requires a pass at –18℃. Figure 8 is just a n example how a pass result looks like. One clearly can see that all four cylinders build up compression – no valve is sticking. Compression in all cylinders: valves open and close without any problems.

Figure 8: Pass Result in CEC F-16-T-96 –

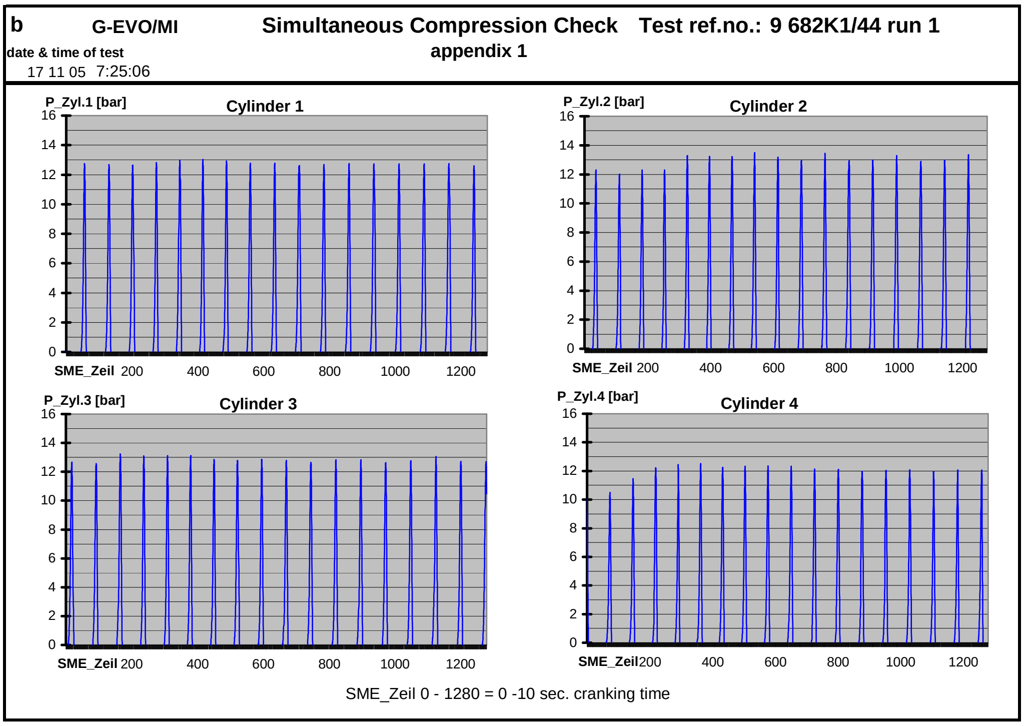
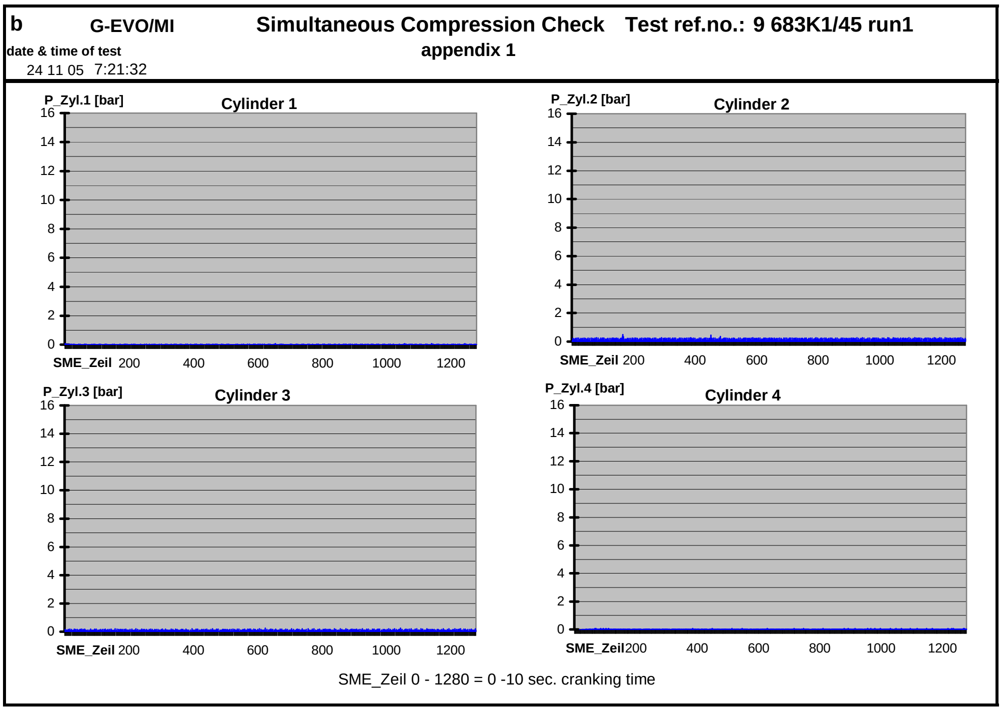


Figure 9 shows a typical fail result. All valves have opened but not closed again. One therefore cannot measure any compression.

Figure 9: Fail Result in CEC F-16-T-96



When we tested a GPA_A at twice the recommended dosage in an European RON 95 at -18 ℃ we got a clear pass result. Surprising ly the same additive failed when it was tested in a blend of the same batch of gasoline but blended with 5 Vol% of a fuel grade ethanol. This was the first indication that well approved additives may fail under severe conditions in ethanol blends (Table 2).

Table 2: Influence of Ethanol on Inlet Valve Sticking in CEC F-16-T-96 at -18℃

GPA_A at 800 mg/kg (twice recommended dosage)	Result
in German Eurosuper without Ethanol	PASS
in Swedish Eurosuper with 5 % fuel grade Ethanol	FAIL

We were, of cause, interested if this again is an effect of ethanol quality or if it is related to the chemical component ethanol. We therefore performed the CEC F-16-T-96 inlet valve sticking test at -18℃ with three d ifferent E5 blends using a German fuel grade ethanol, a US fuel grade ethanol and again a solvent grade ethanol. Since GPA_A failed in all three blends we can conclude that ethanol makes the valve-sticking test more severe (Table 3).

Table 3: Influence of Ethanol on Inlet Valve Sticking in CEC F-16-T-96 at -18℃

GPA_A at 800 mg/kg (twice recommended dosage)	Result
in German Eurosuper with 5 % US fuel grade Ethanol	FAIL
in German Eurosuper with 5 % German fuel grade Ethanol	FAIL
in German Eurosuper with 5 % solvent grade Ethanol	FAIL

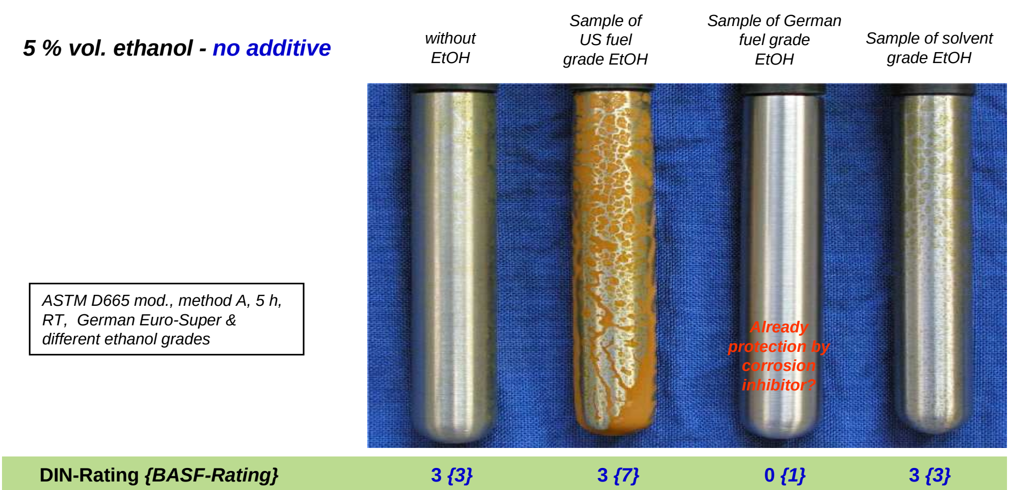
Consequently we developed a new gasoline additive for the Scandinavian market. The new formula gives better protection against valve sticking and corrosion. GPA_B was again tested at –18℃ at twice the recommended dosage (Table 4). It passed the test in all E5 blends. Being aware of the increased risk of valve sticking with ethanol blends it is now possible to adjust the additive formula to the new requirements.

Table 4: Influence of Ethanol on Inlet Valve Sticking in CEC F-16-T-96 at -18℃

GPA_B at 1120 mg/kg (twice recommended dosage)	Result
in German Eurosuper with 5 % US fuel grade Ethanol	PASS
in German Eurosuper with 5 % German fuel grade Ethanol	PASS
in German Eurosuper with 5 % solvent grade Ethanol	PASS
in Swedish Eurosuper with 5 % fuel grade Ethanol	PASS

It is very well known that fuel grade ethanol can have a negative impact on corrosion. For this purpose we usually use the ASTM D665 A protocol running the test at ambient temperature (approximately 20℃) for 5 hours (Figure 10).

Figure 10: Influence of different ethanol qualities on steel corrosion



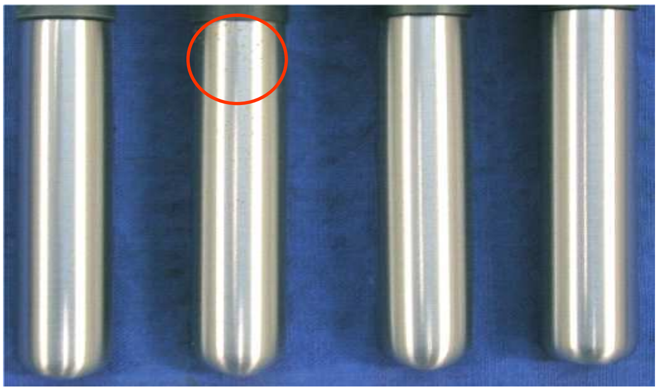
In this test series we see severe corrosion with a sample of an US fuel grade ethanol. The solvent grade ethanol is neutral in this test. Surprisingly a German bio-ethanol sample improved the result. We believe that this fuel grade ethanol has already been additized with corrosion inhibitor. Figure 11 shows that 280 mg/kg of the GPA_B gives perfect corrosion protection for all test gasolines except for the blend with US fuel grade ethanol. However, the rating for this sample is 2 according DIN rating or B+ according NACE rating - a clear improvement.

Figure 11: Influence of different ethanol qualities on steel corrosion

5 % vol. ethanol
280 mg/kg GPA_B

ASTM D665 mod., method A, 5 h, RT, German Euro-Super & different ethanol grades

	without EtOH	*Sample of US fuel grade EtOH*	*Sample of German fuel grade EtOH*	*Sample of solvent grade EtOH*



DIN-Rating *{BASF-Rating}*	**0 *{1}***	**2 *{2}***	**0 *{1}***	**0 *{1}***

Figure 12: Influence of different ethanol qualities on steel corrosion

5 % vol. ethanol
560 mg/kg GPA_B

ASTM D665 mod., method A, 5 h, RT, German Euro-Super & different ethanol grades

	without EtOH	*Sample of US fuel grade EtOH*	*Sample of German fuel grade EtOH*	*Sample of solvent grade EtOH*

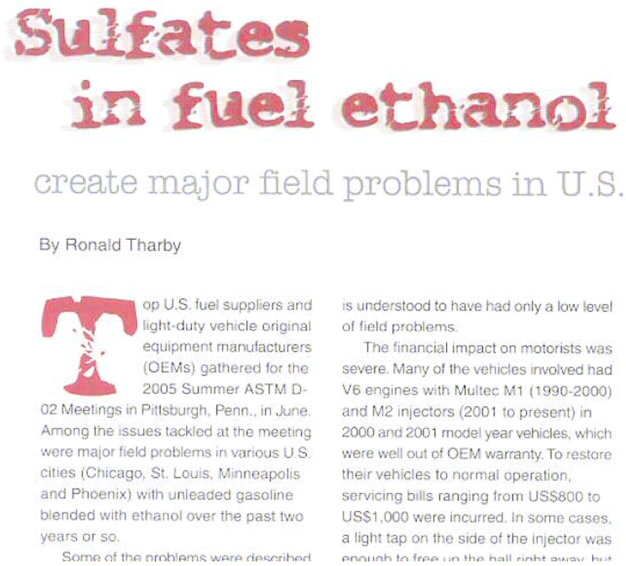
DIN-Rating *{BASF-Rating}*	**0 *{1}***	**0 *{1}***	**0 *{1}***	**0 *{1}***

By increasing the treat level to 560 mg/kg results are perfect (Figure 12), in particular DIN rating is 0 or A according to the NACE rating.

So even if some fuel grade ethanol qualities increase the risk of corrosion this can be controlled by a good gasoline additive. Perfect corrosion protection when additization is adjusted to fuel quality.

A very serious problem is the carry-over of sulphates into fuel grade ethanol. Sulphates are impurities from the bio-ethanol fermentation process being present in amounts up to e.g. 10 ppm. Sulphates are soluble in ethanol at these concentrations but can precipitate when the ethanol is blended with gasoline. Multiple problems have been reported from the US market such as filter plugging in fuel dispensing units and plugging of car injectors (Figure 13). Furthermore we have evidence that some additive technologies have an occasional impact on filter plugging: low molecular weight amines, present in some conventional fuel additives, enhance this problem. Additives which do not contain such amines have no negative or even a positive effect.

Figure 13: Fuel Filter Plugging Problems by Sulphates



Sulfates in fuel ethanol

create major field problems in U.S.

By Ronald Tharby

Top U.S. fuel suppliers and light-duty vehicle original equipment manufacturers (OEMs) gathered for the 2005 Summer ASTM D-02 Meetings in Pittsburgh, Penn., in June. Among the issues tackled at the meeting were major field problems in various U.S. cities (Chicago, St. Louis, Minneapolis and Phoenix) with unleaded gasoline blended with ethanol over the past two years or so.

Some of the problems were described

is understood to have had only a low level of field problems.

The financial impact on motorists was severe. Many of the vehicles involved had V6 engines with Multec M1 (1990-2000) and M2 injectors (2001 to present) in 2000 and 2001 model year vehicles, which were well out of OEM warranty. To restore their vehicles to normal operation, servicing bills ranging from US$800 to US$1,000 were incurred. In some cases, a light tap on the side of the injector was

Last but not least we want to address water related problems with ethanol blends. Ethanol changes the polarity of gasoline and can be extracted to a water phase. This results in increased tendency to form emulsions. Water goes to the gasoline and ethanol goes to the water phase. If the concentration of ethanol changes significantly the octane number will decrease and vapour pressure can increase. In some cases this can lead to off-spec fuels! So, how can we help with additives? It is worthwhile to add dehazer additives to improve phase separation. But even a perfect phase separation will not avoid that water goes into the fuel and ethanol goes into the water. These processes are controlled by thermodynamics whereas phase separation is kinetically controlled.

Why not adding an emulsifier to remove water from tanks and pipelines by forming stable emulsions with gasoline? Beside the fact that this requires significant amounts of additional chemicals this solution will create serious risks: water will be carried to the engines of cars and can cause multiple problems such as corrosion of injectors. It is likely that tanks will be cleaned up and sludge will plug filters and injectors. Since the mentioned water related problems cannot be controlled by additives our recommendation is a good house-keeping.

Summary

It is our experience that some fuel grade ethanol qualities have negative impact both on deposit formation and steel corrosion. However, these problems can be perfectly controlled by modern synthetic GPA's. The impact of ethanol on valve sticking needs to be addressed by the additive suppliers - and mineral oil companies should be aware of it. Carry-over of water in gasoline and vice versa should be controlled by good house keeping; additives can only improve phase separation. Gasoline producers should address the sulphate filter plugging issue. Additive suppliers, however, must not enhance this problem by amine impurities in their products.

Final summary: if you choose the right gasoline performance additive you can significantly improve the performance of your ethanol containing gasoline.

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621.434-632.5	benzinsko/etanolno mješano motorno gorivo	gasoline/ethanol mixed engine fuel
66.022.3	obrada dodavanjem aditiva	treatment by additives
.002.64	gledište svojstava produkta	product properties viewpoint
665.733.5.035	primjenska svojstva benzina	gasoline application properties

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