#### Dave Claydon, Eugen Marko

254

ISSN 0350-350X GOMABN 46, 3, 247-260 Prethodno priopćenje / Preliminary Communication UDK 621.434-632.5 : 665.765.038.2

# THE INCREASING USE OF ETHANOL IN GASOLINE AND THE IMPACT ON THE USE OF GASOLINE DEPOSIT CONTROL ADDITIVES

### Abstract

The use of ethanol in gasoline is growing and this trend will continue well into the next decade. Brazil has been using ethanol for more than three decades and has a well established history of trouble-free use of this component. In the United States the Clean Air Act revisions of 1990 and the reformulated gasoline regulations called for oxygenates in reformulated gasoline. Early on in RFG, most refiners started using MTBE because it could be blended in easily at the refinery, and because it did not have the volatility problems that ethanol has. However, due to the unexpected taste and odour problems found in groundwater while using MTBE, this option has become far less popular. This means ethanol has gained acceptance as an oxygenate and blend component for gasoline.

In the United States the use of inlet valve deposit control additives is mandated and this means that when Ethanol becomes an accepted gasoline blend component the effect this has on additives must be given some priority. Similarly in most parts of the world it is common practice to use multifunctional detergent based additives in gasoline in order to allow oil companies to market differentiated quality at the forecourt.

This paper discusses studies conducted by Afton Chemical to ensure that existing gasoline additive chemistry is able to give optimum performance in gasoline containing different percentages of Ethanol. At the same time an investigation has been conducted to understand the need to develop different additive chemistries to deal with the changing gasoline quality.

goriva i maziva, 46, 3 : 247-260, 2007.

# Introduction

Ethanol is the most widely used renewable fuel oxygenate used to meet current gasoline specifications. The quality of acceptable ethanol is controlled by the ASTM D4806 specification.

Most contemporary petrol cars will run on gasoline containing a 10% mixture of ethanol to petrol and many major car manufacturers have developed cars which run on fuels containing higher proportions of alcohol, typically E85. Ethanol has properties which are different from petrol; for example it has a higher octane rating, is more corrosive, cleans the old deposits away (hence filters may need changing after a short time, initially) and can make engine starting more difficult, especially at low ambient temperatures.

Blending Ethanol into gasoline will affect the octane levels, oxygen content, volatility and water solubility. Testing shows that the addition of 10% Ethanol will increase the RON of gasoline by 3-4 numbers. Ethanol will increase the vapour pressure of the gasoline and also decrease the 50% volume distillation temperature. High volatility can cause hot drive ability issues and low volatility will have an affect on low temperature starting of the vehicles. Inclusion of ethanol into gasoline will affect both high and low volatility The presence of ethanol in the gasoline will adversely affect the gasoline water separation and therefore it is important to focus on improved housekeeping and elimination of water from tanks and the distribution system.

The solvency effect of Ethanol, especially when used at high levels, will loosen rust, dirt etc from the tanks and distribution system and this could lead to filter blockage at certain points through the distribution system. Most current gasoline vehicles in the European market would not contain elastomers and gaskets that are compatible with high levels of ethanol and this would be a concern. Since 85% ethanol containing gasoline is commercially available in Southern Sweden both SAAB and Volvo have ensured that their new gasoline vehicles are able to handle these fuels but not all vehicles on the market would be compatible.

### Car manufacturers position on use of Ethanol in gasoline

Most car manufacturers support the use of gasoline containing up to 10% ethanol provided the resulting blend meets the requirements of the EN228 gasoline specification.

With the escalating cost of fuel, many customers are considering whether they would be able to use E-85 fuel in non-E85 compatible vehicles. Only vehicles designated for use with E85 should use E85 blended fuel. E85 compatibility is designated for vehicles that are certified to run on up to 85% ethanol and 15% gasoline. All other gasoline engines are designed to run on fuel that contains no more than 10% ethanol. Use of fuel containing greater than 10% ethanol in non-E85 designated vehicles can cause driveability issues, service engine soon indicators as well as increased fuel system corrosion.

goriva i maziva, 46, 3 : 247-260, 2007.

At the present moment most market experience in using high levels of ethanol are to be found in the Brazilian market. In 1975 ethanol was first introduced into the Brazilian market at a level of 12% in gasoline. There were major field problems such as corrosion, deposits and starting difficulties at low temperatures. These problems were overcome by co-operation between oil companies, additive companies and car manufacturers. In 2005 more than 1 million cars on the Brazilian market have been designed to operate on "flex fuels" which are fuels containing from 25 to 100% ethanol. The reason this is possible is related to improvements in the infrastructure and the vehicle designs. This includes upgrading the materials of construction used with fuels containing ethanol. The introduction of electronic injection in cars so that they can manage any percentage of oxygenates. As a consequence there are no reported field problems related to the use of "Flex fuels" in the Brazilian market.

At the present moment there are only a limited number of vehicles in the European car Parc that would be able to safely operate on gasoline containing more than 24% ethanol.

It is strongly recommended to only use E85 gasoline in vehicles which are on the list of approved vehicles for use with E85 gasoline.

### The use of detergent additives in gasoline containing ethanol

Testing in standard engine tests has shown that introducing ethanol into standard gasoline will have a tendency to increase inlet valve deposits. This can, of course, be addressed by using a premium quality fully formulated gasoline detergent additive such as HiTEC 6421. In some cases the treat-rate may increase as levels of ethanol increase in the base gasoline blend. Afton Chemical has conducted engine testing to evaluate the impact of ethanol on inlet valve deposits in gasoline containing up to 24% ethanol. The tests were conducted in the USA using the standard Ford 2.3I engine test procedure. The results are shown below:



goriva i maziva, 46, 3 : 247-260, 2007.



The results show that HiTEC 6421 can easily compensate for the increased levels of inlet valve deposits that arise in base fuels containing ethanol.

In addition to demonstrating good performance benefits when using additives in gasoline it is essential that all commercial gasoline additives are robustly tested for their "no harm" effects.

HiTEC 6421 has been evaluated for impact on combustion chamber deposits in gasoline containing up to 24% ethanol. It is a known fact that all commercial gasoline detergent chemistries will contribute to combustion chamber deposits but these additive packages are formulated to minimise the contribution. The graph shown below indicates that the presence of up to 24% ethanol in the gasoline does not adversely affect that contribution of HiTEC 6421 to combustion chamber deposits when compared with a gasoline containing no ethanol.



HiTEC 6421 Treat Rate, ppm v/v

### The problem of sulphates in ethanol

In addition to the testing conducted above a fairly extensive investigation was conducted in the United States due to indications that certain commercial detergent additive chemistries were causing problems when used in gasoline containing 10% ethanol. The problems manifested themselves in service station filter blocking and fuel injector sticking. The problem was highlighted when the 10 micron filters fitted to filling station pumps in the US and Canada showed premature plugging. In severe cases the filters had to be replaced daily rather than the normal 3-6 months intervals. Customers complained that it was taking longer to fill their vehicles.

An investigation was conducted to try to find the cause of the filter blockage and first indications pointed to the presence of ammonium and sodium sulphates in the

goriva i maziva, 46, 3 : 247-260, 2007.

deposits. Further analysis showed that sulphates are often found in fuel-grade ethanol but seldom in gasoline. Sulphate levels as high as 4-7ppm were found in ethanol samples linked to the filter blockage problems. In order to better understand this issue the industry designed a bench filtration tests designed to correlate with the filtration system used in a service station pump.

The bench test was designed to use the actual filter media used in service station pumps. Tests were then conducted using realistic levels of ethanol and sulphate concentrations mimicked the levels seen in the market. The tests were accelerated by increasing the flow rate through the filter but maintaining a realistic pressure drop. The test cycle was designed to simulate filtration of 50000 gallons of gasoline at the service station.

The rig was used to test the effect of adding different qualities of commercial ethanol to gasoline treated with detergent additives. The tests indicated that there were no indications of filter blockage when testing 100% commercial gasoline treated with well established commercial detergent additives. The addition of certain grades of commercial ethanol to the same quality of commercial gasoline at a level of 10% had a negative impact on filterability. The graph shows this impact:



Similar testing has been conducted to compare the filterability impact of using different gasoline detergent chemistries. The results, shown below, indicate that some products are more prone to this phenomenon than others:

Based upon this comparative study the industry has developed new additive packages which are known to be neutral in terms of interactions with any sulphates

goriva i maziva, 46, 3 : 247-260, 2007.

present in commercial ethanol. Although we believe that, by controlling the sulphate content in commercial ethanol, the filterability problem can be greatly improved, the industry have developed gasoline detergent additive packages which will not be affected by the presence of sulphates in ethanol.

The graph shown demonstrates the performance of the new gasoline additive technology:



### goriva i maziva, 46, 3 : 247-260, 2007.

## Conclusion

The inclusion of ethanol into commercial gasoline can cause an increase in deposit formation on inlet valves of port fuel injection gasoline engines. Existing gasoline detergent chemistry can dramatically reduce the levels of deposits formed. The use of gasoline detergent additives in gasoline containing ethanol up to 24% does not dramatically increase combustion chamber deposits.

In response to a field problem experienced in the United States and Canada the industry have conducted a study to investigate the cause of filter blockage at service stations when gasoline containing ethanol has been used. The investigation involved developing a bench filtration rig which has been instrumental in gaining a better understanding of the cause of this problem. The problem appears to be related to the presence of insoluble sulphates in commercial ethanol. The investigation indicated that a number of existing gasoline detergents additives interact with the sulphates to cause severe filter blockage.

The industry have developed and evaluated gasoline detergent additives that give optimum performance in gasoline containing up to 24% ethanol. Testing has also confirmed that these products will not cause operational problems either in the gasoline engine or the gasoline distribution system.

Flex fuel is becoming increasingly available in the European market and many additive companies are conducted studies in order to determine the performance features that can be improved by the use of additives.

UDK	ključne riječi	key words
621.434-632.5	benzinsko/etanolno miješano	gasoline/ethanol mixed engine
	motorno gorivo	fuel
665.765.038.2	detergentno disperzantni aditiv	detergent-dispersant additive

#### References

- (1) ASTM D4806-United States specification controlling Ethanol quality
- (2) Ethanol/gasoline overview-Ron Fricke-Afton Chemical Corporation February 2005. SAE paper 2005-01-3864 "Gasoline driveability index, Ethanol content and cold start/warmup vehicle performance by Carlton Jewitt, Lewis Gibbs & Beth Evans.
- (3) "Specific Bioethanol issues for the automotive industry" John Bennett-Ford motor company presentation at the International conference on biofuel standards, 27<sup>th</sup>-28<sup>th</sup> February 2007 in Brussels.
- (4) Ethanol as octane enhancer & fuel extender-The Brazilian experience. Presented by Sergio A.M. Fontes of Petrobras at the ARPEL workshop in Jamaica, March 30<sup>th</sup> 2004

(5) Understanding impurities in Ethanol blended gasoline-Ethyl petroleum additives-2004

### Authors

Dave Claydon, e-mail: David.Claydon@AftonChemical.com

Eugen Marko, e-mail:Eugen.Marko@AftonChemical.com

### Received

13.9.2006.

260

goriva i maziva, 46, 3 : 247-260, 2007.