Synthetic Alcohols: The Sasol Experience With Fischer-Tropsch Gasoline/Alcohol Blends And A Comparison With The Behaviour Of Fischer-tropsch Gasoline/ Bio-ethanol Blends

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Abstract:

Sasol produces several transportation fuels in South Africa via its proprietary High Temperature Fischer-Tropsch (HTFT) process. The final fuel product slate consists mainly of gasoline, diesel and kerosene. During the production of fuel by the HTFT technology several chemicals, including alcohols, are also produced. The alcohols consist mainly of ethanol while several higher alcohols, from propanol to hexanol, are also produced during the process.

The demand for alternative fuels increased significantly over the past few years. In this regard, bio-ethanol has received significant attention as a gasoline blend component in the quest to become less dependent on crude oil-derived sources and in pursuit of cleaner fuels. The availability of bio-ethanol may increase in South Africa and it is therefore important to understand its behaviour in blends. Sasol has extensive experience with synthetic gasoline/FT ethanol blends throughout the logistical system, and is therefore in an ideal position to ensure smooth market entry of bio-ethanol/gasoline blends.

Alcohols, especially the higher alcohols (n-propanol, n-butanol and n-pentanol), are known to be corrosive to fuel system components (older carburettors and certain fuel system components in modern cars). Either these higher alcohols need to be limited in the fuel ethanol or the corrosion behaviour needs to be effectively controlled by additive addition. As Sasol fuel ethanol initially contained higher alcohols, several studies were carried out over the years by Sasol in order to understand the corrosion inhibitor additisation requirements of gasoline/alcohol mixtures. Another requirement of these alcohol containing fuels to be fit for purpose is the additisation with detergent additive packages in order to control inlet valve cleanliness. In this paper the Sasol experience with Fischer-Tropsch gasoline/alcohol blends will be discussed, summarising experiences over the past 30 years. The focus will mainly be on the optimisation of corrosion inhibitor additive packages for these fuels. Alternative test methods, specifically developed over the years to characterise the corrosion behaviour of fuels, will also be discussed.

In this paper, a comparison is made between the corrosion behaviour of Fischer-Tropsch gasoline/synthetic ethanol blends and Fischer-Tropsch gasoline/bio-ethanol blends. The wet and dry corrosion properties of bio-ethanol and synthetic ethanol, when blended with a synthetic base gasoline with a Research Octane Number (RON) of 95, as well as the performance of commercially available detergent packages in these fuels are summarised. Corrosion studies were carried out using a mini Dynamic Alcohol Corrosion (DAC) test method, as well as the conventional wet corrosion method (ASTM D665). The results with regards to wet and dry corrosion of the synthetic HTFT-produced RON95 blends, containing up to 10 volume % synthetic alcohol or bio-ethanol, are discussed. The additisation properties of the bio-ethanol/gasoline and synthetic ethanol/gasoline blends are described using a combination of commercially available corrosion inhibitors and other additive packages. Some evaluations employing full scale engine tests were carried out in order to establish any possible differences between the detergent additive requirements of FT gasoline/bio-ethanol and FT gasoline/synthetic ethanol mixtures.
Synthetic Alcohols: The Sasol Experience With Fischer-tropsch Gasoline/Alcohol Blends And A Comparison With The Behaviour Of Fischer-tropsch Gasoline/Bio-ethanol Blends

1. Introduction

The demand for alternative fuels for application in internal combustion (IC) engines has increased significantly over the past few years with security of supply, an ever increasing international vehicle fleet and the move towards renewable, more environmentally friendly fuels as the main drivers in automotive fuel applications. In recent years, bio-ethanol has gained importance as a possible alternative to crude oil-derived fuels [1] in spark ignition engines. Although the ‘food versus fuel’ debate gained momentum as a possible threat to further market penetration of biofuels, alternatives to crude-derived fuels are limited and biofuels currently present the most likely avenue to non-crude based, renewable fuels. Bio-ethanol, derived from the fermentation of corn, sugar and other natural products, has been used for a long time in gasoline systems, and has been used in varying blend ratios in countries like South Africa, Brazil, the USA and European countries to supplement current gasoline supply. Alcohols present several advantages when blended with conventional gasoline, including a significant reduction in several regulated and unregulated emissions as well as octane benefits. Over the years, several in-depth studies have been conducted to assess the effect of ethanol as a gasoline extender [2, 3, 4]. However, currently more in-depth consideration is given to the greenhouse gas footprint and, where bio-ethanol was previously considered as a green, renewable fuel extender, factors such as the type of biomass and the way in which these crops are grown are now also under serious scrutiny. Although bio-ethanol has been studied as a diesel extender [5], its use in diesel engines is currently limited. Ethers may be more promising as a diesel extender [6].

As South Africa does not have any known crude oil reserves, a major portion of fuel in the inland area is derived from coal, using Sasol’s unique Fischer-Tropsch based processes. In South Africa, around 11.5 billion litres of unleaded gasoline and around 10 billion litres of diesel were consumed during 2007 [7]. Currently, around 27% of the South African liquid fuel supply originates from synthetic fuels, produced at the Sasol Synfuels refinery, situated in Secunda (based on coal-to-liquids technology) and the PetroSA plant in Mossel Bay (based on gas-to-liquids technology).

In South Africa, a 90 million litre per year bio-ethanol from sugar-beet plant is currently under consideration. Although South Africa is well experienced in the use of synthetic ethanol, current experience on the inclusion of bio-ethanol in the South African fuel pool is limited. An extensive amount of information is available in the open literature on crude-derived gasoline/ethanol blends, but no information exists on synthetic gasoline/bio-ethanol performance, especially with regards to its additive requirement.

The extensive experience gained by Sasol over the years with handling synthetic ethanol (Sasol Fuel Alcohol) in gasoline includes managing the transport of ethanol in pipelines, understanding blending behaviour and understanding end-use applications. This article aims to provide an overview of the extensive Sasol experience with ethanol blends and summarises the aspects that are required to ensure problem-free use in the market. Over the years, the composition of Sasol Fuel Alcohol has also changed, addressing some of the earlier experiences with this alcohol. The lessons learnt from the introduction of synthetic ethanol will be useful for the potential introduction of bio-ethanol in South Africa, while recognising that the nature of synthetic ethanol and bio-ethanol may be slightly different.

In this article an overview is given of the South African experience with synthetic ethanol/synthetic gasoline mixtures, and a comparison of the additive requirements of these mixtures with synthetic gasoline/bio-ethanol mixtures. Generally gasoline requires the addition of corrosion inhibitor additives and ethanol-containing gasoline fuels (crude derived and synthetic) are no exception. The main focus of the experimental part of this article will be an assessment of corrosion
inhibitors in gasoline/ethanol blends, but will also briefly discuss inlet valve deposit control using commercially available deposit control additive packages. Several combinations of crude-derived gasoline in blends with bio-ethanol and synthetic ethanol respectively, will also be discussed. An overview is also given of test method developed at Sasol, specifically for ethanol-containing gasolines.

2. Effects Of The Addition Of Ethanol To Gasoline On Fuel Quality

The addition of ethanol to gasoline introduces several benefits to the fuel, including a reduction in regulated emissions [2]. However it should be noted that certain unregulated emissions such as formaldehyde increase [8]. It is expected that these aldehydes will be further oxidised in vehicles equipped with catalytic converters. The increases in aldehydes are however, very small compared to the potential reduction in regulated emissions. Typically, ethanol blends can be stored, transported and handled by conventional fuel distribution systems. Depending on the ethanol content of the blend, special precautions are required—these include different water management systems and fire fighting systems. Ethanol blends can be used in conventional gasoline engines, although higher alcohol concentrations may require changes to the engine hardware. Several studies were carried out in the 1980's to qualify and investigate the effect of bio-ethanol as a gasoline blending component [2]. As an example of a major study, work was carried out in 1984 to evaluate the effect of 10% bio-ethanol in a regular unleaded fuel on vehicle operability [2]. Generally, no effect was noticed on the lubricant performance and vehicle driveability in carburettor-equipped vehicles.

With the introduction of ethanol into gasoline, it is important to consider the effects of ethanol on the gasoline properties [3, 9]. However, many of these aspects can provide potential benefits to the fuel supplier.

1. Ethanol addition to gasoline can provide emissions benefits. Several regulated and particulate matter [PM] emissions are significantly reduced by the addition of ethanol to the gasoline [8].

2. The Reid Vapour Pressure (RVP) of ethanol/gasoline blends is higher than that of conventional gasoline. It is common practice in ethanol fuels to adjust specifications in order to accommodate this.

3. Ethanol has a good blending octane number, which may provide a potential benefit to a gasoline fuel.

4. The heat of combustion of ethanol is typically lower than that of conventional gasoline. This may also be a potential benefit given the lower temperatures in the combustion chamber.

5. Corrosion aspects—Material compatibility testing was carried out over the years and several commercial corrosion inhibitors exist that improves the corrosion properties of a fuel. It must also be taken into account that unadditised conventional gasoline may also be corrosive by itself.

6. Other issues such as fuel economy, driveability, oil drain intervals and fuel system deposits have been investigated. These effects are engine technology and fuel alcohol content dependent [11].

3. Ethanol Use In South Africa

In South Africa, bio-ethanol was used in the 1950's and 1970's as a fuel/fuel component. This was marketed as 'Union Spirits' but was only available in coastal areas. However, the ethanol that is currently used in the South African fuel pool is obtained from the Sasol Synfuels plant in Secunda, where it is produced as a co-product of the Fischer-Tropsch process. The Fischer-Tropsch process also produces higher alcohols, therefore the ethanol stream could also contain low percentages of heavy alcohols from propanol up to pentanol. Previous work [3, 9] has indicated that similar blending octane values were obtained with synthetic ethanol as with bio-ethanol. Synthetic ethanol has been used since 1981 in blends to supplement the gasoline supply to the inland areas. The composition of this synthetic ethanol, known as Sasol Fuel Alcohol (SFA) has also changed over the years in order to address earlier corrosion related issues.
experienced in the South African market.

As with any gasoline component, it is also important to ensure that ethanol blending is carried out correctly. Over the years Sasol has gained significant experience in this regard. This experience includes blending and blend practices of ethanol at depot level as well as splash blending. Pipeline distribution is an important means to distribute ethanol in the South African inland area. Extensive trials were carried out to ensure compatibility of the gasoline/alcohol blends in the pipeline network. Two very interesting phenomena were observed during the initial pipeline trials. In the first case, when a gasoline/alcohol mix was initially conveyed via the pipeline, discolouration of the front end of the gasoline/alcohol slug was noticed. This was attributed to an iron/metal deactivator complex. It was also observed that the ability of the gasoline/alcohol mixture to dry out residual water adhering to the pipeline was higher than anticipated. Several changes to refinery hardware and operating procedures including pipeline procedures were undertaken to prevent these problems from occurring and the experience gained in this regard has ensured problem-free transport of gasoline/ethanol blends in the South African fuel distribution network.

Initially the main challenge with the use of SFA (containing higher alcohols) in gasoline was with corrosion, observed particularly in carburettor-equipped cars in the early years when 8 to 12% SFA blends were used in South Africa. Already in 1981, Armscor, a South African company, reported experiencing corrosion problems when operating vehicles on a synthetic alcohol/gasoline mixture [12]. They proposed possible solutions to this problem, including using more corrosion resistant materials or the use of corrosion inhibitors. The corrosion challenges were overcome by the use of commercially available additives such as mono ethylene glycol (MEG) in combination with commercial anti-corrosion additives. The SFA used during this time, however, contained significant amounts of higher alcohols, known to be responsible for corrosion. The composition of SFA has changed significantly over the years in order to minimise the corrosion potential of SFA in gasoline matrices. It is important to note that the majority of problems experienced during the early years were mainly related to the presence of n-propanol. n-Propanol was shown to be especially corrosive towards the aluminium components found in carburetors [13]. This effect was exacerbated by the (then) use of tetraethyl lead, which contained bromine scavengers. Lead additives were however, phased out from the South African fuel pool in 2006, so this is not a concern anymore. A number of different Sasol alcohols have been tested subsequently with the major conclusion that little differences were found between the corrosion of ethanol with purities in excess of 95% ethanol, when used in blends with gasoline.

Due to new export markets opening up for the South African synthetic alcohol, between 1994 to 1999, ethanol was removed from the Sasol fuel pool. However, oversupply of this ethanol occurred in export markets, and therefore, synthetic ethanol was reintroduced into gasoline in 1999, initially at 10 volume %, and then gradually reduced to 8% and eventually 2%.

4. Experience With The Use Of Sasol Fuel Alcohol (SFA)

One of the aspects that need to be considered for fuels is the prevention of corrosion. Corrosion can mainly classified into a) wet corrosion (the corrosion behaviour in the presence of water) and b) dry corrosion (corrosion in the absence of water).

In subsequent testing, carried out with synthetic ethanol addition to a synthetic base fuel, it was found that a commercially available corrosion control additive was effective in controlling corrosion, when used in combination with MEG. In the absence of the corrosion control package, it was found that corrosion was evident in the mini-DAC corrosion test (discussed in Section 5.3). Experience in the early 1970's indicated that synthetic ethanol at 1% addition did not result in any aluminium corrosion, but 2% ethanol required MEG...
addition. However, it was not possible to control corrosion with the addition of MEG alone. This was confirmed in a later study, where MEG was unable to control corrosion in a 2% ethanol/synthetic leaded base fuel [4].

Another important parameter to consider in order for these gasoline/alcohol mixtures to be used as a gasoline extender is the deposit forming tendency of the fuels. Ethanol-containing fuels are no different to conventional gasoline and require additisation of deposit control additive (DCA) packages in order to minimise deposits. Commercially there are several DCA packages available. These additives are added to all gasoline in order to ensure that the fuel system, including the valves and injector nozzles, remains clean.

Commercial deposit control additives were evaluated and it was shown that the deposit forming tendency of these gasoline/alcohol mixtures could be effectively controlled using commercially available additive packages [14].

4.1 Additives and corrosion control

One of the considerations when using ethanol in gasoline blends (irrespective of the origin, i.e. bioethanol or synthetic ethanol) is the formation of rust, i.e. water induced corrosion. As ethanol is hygroscopic, it can take up water, which could increase corrosion problems. The solubility of the ethanol in the base fuel decreases, which results in phase separation occurring. This ethanol/water mix is then highly corrosive. Even without phase separation, the presence of small amounts of acetic acid, acetaldehyde and n-propanol could contribute to corrosion.

Several chemistries have been used as the basis for corrosion inhibitors, for use in fuel systems. For example, alkyl or alkenyl succinic acid [10] and hydrocarbyl succinic acid or anhydride [15] were shown to be effective against the corrosion of steel, zinc casting alloy and tin/lead alloy. Aliphatic dicarboxylic hydrocarbons were also effective against corrosion of these alloys [16]. Etheramines, such as decyl oxypropylaminopropylamine, were shown to be effective against iron strip corrosion [17]. Reaction products of benzothiazole, formaldehyde and n-alkyl propylene diamine were also shown to be effective in gasoline/ethanol blends [18]. Other chemistries include [11, 19] amines, etheramines, imidazoles, thiadiazoles, carboxylic acids [9], p-phenylene diamines, dicycolhexamine, alkyl succinic anhydrides and mixtures and salts thereof.

4.2 Additives and deposit control in synthetic fuel/SFA mixtures

It is known that the addition of alcohols to gasoline may potentially increase inlet valve deposits. In previous work conducted using the CEC F-05-93 test method, the effect of SFA in a synthetic base gasoline on inlet valve deposits was evaluated [3, 9]. During testing, it was evident that there was very little change in the overall inlet valve deposits as a function of ethanol content, and the fuel was generally treatable with commercially available detergent additive packages to reduce the deposits to acceptable norms.

5. Corrosion Testing Of Fuel Alcohols

Under certain conditions, particularly at high temperatures, gasoline/ethanol mixtures may react with the aluminium components used in older carburettor-equipped vehicles. In order to quantify the influence of ethanol on fuel corrosivity, extensive work was carried out in the 1980's and 1990's in South Africa to ensure that these gasoline/synthetic ethanol blends could be used effectively in vehicles. Several different test methods have traditionally been applied to predict the anti-corrosion performance of ethanol/fuel blends. Measurements on weighed metal coupons [15] can be used to assess anti-corrosion performance of blends. In this test, the weighed coupons are exposed to the fuel at 43 °C for 14 days. After the test period, the coupons are removed from the fuel and cleaned of corrosion product. The samples are then weighed to determine the weight loss, which is indicative of the amount of corrosion. Iron strip corrosion is another test that is applied to study corrosion. In this test, an iron strip is exposed to the test fuel, for a period of 15
minutes, and the degree of rusting is then determined visually [17].

5.1 Carburettor bench testing

A laboratory scale carburettor bench setup was developed at Sasol in order to test a fuel's corrosiveness and the effect of corrosion inhibitors on metallic components, typically found in vehicles equipped with carburettors (Figure 1). In this setup, most off-the-shelf carburettors could be evaluated. During the test, the carburettors are exposed to fuel in 30 minute cycles. The fuel temperature is maintained at 85 °C, and fresh fuel is pumped to the carburettors every 30 minutes. The flush period is around 3.5 minutes. Heat soaking is then applied to the carburettor setup. The test is run over a period of 500 hours, after which the carburettors are disassembled and evaluated visually for corrosion damage. This test method was not used as part of the current study.

Although most modern vehicles are equipped with fuel injection systems, carburettor cars are still prevalent in the South African market, and adequate protection against corrosion is required for these vehicles. It was found that the majority of carburettor corrosion occurred after operation during the heat soak cycle.

5.2 The Dynamic Alcohol Corrosion (DAC) test

Due to the high operating cost and complexity associated with the carburettor bench test, it was necessary to develop a less expensive and less time consuming technique to study alcohol corrosion. The dynamic alcohol corrosion (DAC) test was therefore developed to simulate exposure to alcohol containing fuels, as well as to simulate the heat soaking cycles associated with repeated stop/start operation (Figure 2).

The DAC setup consisted of several reactors, which could be used to test the corrosion behaviour of several fuels at the same time. Although this setup worked well, it still occupied a considerable amount of space and consumed a considerable quantity of fuel. Improvements were therefore considered in order to make it less labour intensive and less expensive to operate.

Up to early 1987, the aluminium alloy SA-18 was used to manufacture all test coupons used for corrosion tests on alcohol-containing gasoline conducted by Sasol Oil R&D. At that time, certain vehicle models were found to be more sensitive to carburettor corrosion [3]. Metal analysis of these corrosion-prone carburettors was carried out by SIB (Scientific Investigation Bureau) and it was found that the aluminium alloy LM-24 (BS1490: 1988) was more representative of these carburettors than SA-18. Of importance was the Cu and Zn-content of LM-24, which was closer to those in...
the sensitive carburettors, as well as the Al-content of 87.0%, which is also more representative of the Al-content in these sensitive carburettors. The metal analysis results are shown in Table 1.

<table>
<thead>
<tr>
<th>Element, (Mass %)</th>
<th>Carburettor 1</th>
<th>Carburettor 2</th>
<th>SA 18</th>
<th>LM-24</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>87.5</td>
<td>88.0</td>
<td>83.4</td>
<td>87.0</td>
</tr>
<tr>
<td>Copper</td>
<td>3.0</td>
<td>2.7</td>
<td>3.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Zinc</td>
<td>2.4</td>
<td>2.6</td>
<td>1.0</td>
<td>2.5</td>
</tr>
<tr>
<td>Iron</td>
<td>1.4</td>
<td>0.9</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The LM-24 was subsequently used as test coupons in all alcohol/aluminium corrosion tests, including the newly developed DAC test. During the rest of the 1980’s, various carburettors and metallic fuel system components from the market were analysed for their metal composition. Most of these were parts from vehicles which had been found to be sensitive to fuel system corrosion in some or other respect.

5.3 Mini DAC test

An improvement on the DAC method was made when an apparatus, known as the mini DAC, was developed. In the mini DAC test, a specimen comprising of the aluminium alloy or an actual vehicle component is exposed to a continually refreshed gasoline/alcohol mixture. During the test, the mini reactor is filled with fuel, heated to constant temperature and drained [20]. The test setup is kept at 80 +/- 2 °C. This type of exposure was found to be representative of the worst case scenario of the heat soaking cycle that occurs in the engine after it has been switched off. The test is carried out over a period of 50 hours, which is equivalent to 1000 normal driving cycles.

This mini DAC test determines the extent to which the aluminium components in a vehicle’s fuel system would undergo corrosion when in contact with the gasoline/alcohol fuel blend. It has been found previously that the carburettor corrosion occurs mainly during the high temperature heat soak period (in excess of 75 °C). During normal driving, temperatures in the carburettor were seldom found to exceed ambient temperature but, during heat soaking, these temperatures were shown to increase dramatically.

A photo of the DAC setup is given in Figure 3.

Figure 3: Mini-DAC experimental setup for testing alcohol corrosivity

Typical applications for this test method include:

1. Determination of the relative corrosivity of different fuels.
2. Assessment of the tendency of different aluminium components to undergo corrosion.
3. The evaluation of the effectiveness of corrosion inhibitors in preventing fuel system corrosion.

The mini DAC test yields a largely qualitative result, which is an indication of whether or not corrosion is visible. The type and extent of the corrosion is also noted. The determination is based on a visual assessment, and the percentage of the surface area corroded during the 50 hour period is reported.

5.4 Correlation of DAC results with vehicle operability

Studies were also carried out by Sasol to correlate the actual vehicle experience and the results of the DAC and carburettor bench tests. In this study, laboratory
results were compared with corrosion in several potentially corrosion-sensitive South African vehicles that were typically used for town and freeway driving. A Sasol SFA, added at 10% to a leaded base fuel, was used in all testing. It was found that the corrosion on the DAC and carburettor bench test could be directly correlated with corrosion found in corrosion-sensitive vehicles. It was also concluded that all three of these test methods were sensitive to corrosion in the presence of anti-corrosion additives [21]. It was also found that two commercial anti-corrosion additives, evaluated in this study, were highly effective in controlling corrosion in corrosion-sensitive vehicles.

5.5 Wet corrosion testing

It is important that the fuel is non-corrosive to pipelines and other metal surfaces. ASTM D665 (or modifications to the method) is used for the assessment of the wet corrosion (i.e. corrosion in the presence of water) properties of a fuel. The aim of this test is to evaluate the anti-rust properties of these fuels under specified conditions relating to temperature, stirring rate, and water content. The test is also used to evaluate the effectiveness of corrosion inhibitors and as a tool to optimise corrosion inhibitor concentrations. The test evaluates the extent to which rust forms on a cylindrical steel rod, whilst immersed in a mixture of 300 ml fuel and 30 ml water, at a temperature of 40 °C. The test is run over a period of 3 hours during which the immersed steel rod is rotated every 15 minutes. At the end of the test, visual inspections are undertaken to assess the extent of corrosion. The test is carried out in duplicate. A sample is classified as failing, if rust appears on both test rods at the end of the three hour period. The percentage of surface rust detected is used to rate the propensity of rusting of the fuel.

5.6 Other additive requirements: Deposit Control Additives and Inlet valve deposit (IVD) testing

The tendency of a fuel to form deposits is usually evaluated using the European Industry Standard procedure, described by the Coordinating European Council (CEC) protocol F-05-93, using a Mercedes M102E engine [22]. The majority of the inlet valve deposits formed during this test is due to the fuel, however, the lubricating oil also contributes. Deposit control additives are typically used to clean up inlet valves, however, the use of these additives may result in either increased or decreased deposits in the combustion chamber. In alcohol-extended gasolines, fuel composition, alcohol content and detergent additive chemistries are known to influence deposits [22]. There is evidence that gasoline-containing ethanol may result in higher levels of engine deposits, especially on the intake valves [21]. Second generation port fuel injected (PFI) detergent additives in gasoline/alcohol blends were also shown to exacerbate the problem. As these deposits may be linked to decreased driveability (higher octane demand) as well as disrupting fuel flow to the cylinder, it is of the essence to limit the levels of these deposits in internal combustion engines. Careful optimisation of both the additive chemistries and the treat rates are required to ensure optimum deposit control in internal combustion engines. It is however known that the carrier oil in DCA additives may contribute to deposits, so careful optimisation is required.

Based on the understanding gained and described in the first part of the document, evaluations were carried out in order to assess the effect of ethanol in synthetic and crude derived matrices.

6. Experimental

The main objective was to investigate if there was any significant difference in corrosion behaviour between synthetic ethanol and bio-ethanol in synthetic gasoline matrices. In order to compare the corrosion behaviour of synthetic ethanol and bio-ethanol, several laboratory blended synthetic gasoline fuels were selected for evaluation. Wet and dry corrosion properties of the fuels were investigated. The fuel contained no performance or corrosion additives.

As a second part of the in investigation, the inlet
valve deposit formation potential of different bio-ethanol and synthetic alcohol-containing blends were also evaluated. The main focus was on a synthetic gasoline matrix, as this is not yet described in literature. For this study, the IVD tests were performed according to an in-house developed test method that is similar in nature to the Coordinating European Council (CEC) test method (CEC F-05-93). These test methods were designed to evaluate the propensity of gasoline or gasoline additive formulations to prevent IVD’s in fuel injected engines [13].

6.1 Fuels used in this study

6.1.1 Fuels used in the experimental evaluation work

The following synthetic fuels were used in the experimental evaluations:

1. Synthetic base fuel, (RON 95, MON 84) prepared by laboratory blending
2. Synthetic base fuel containing 10 % bio-ethanol, using the same laboratory blended base fuel
3. Synthetic base fuel containing 10% SFA, using the same laboratory blended base fuel
4. Synthetic base fuel containing 10% Sasol 99% pure synthetic ethanol (also known as ethanol lights), using the same laboratory blended base fuel

The synthetic base fuel was blended in the laboratory from synthetic gasoline fuel streams in order to simulate a RON 95 synthetic gasoline. The synthetic base gasoline had a RON value of 95 and a MON value of 84. Although the MON of this laboratory blend was slightly lower than the crude derived base fuel, MON was not considered to be critical in evaluation of the corrosion control additives. The two alcohol-containing fuels were similar in octane value and approximately 2.7 octane units higher than the base fuel. The effect of the ethanol addition could be seen in the Fuel Volatility Index (FVI) values, which was significantly higher than the base fuel. Most other fuel properties were influenced to a lesser extent by the addition of ethanol. For testing of the corrosion inhibited fuels, the base fuels were additised with a commercial corrosion inhibitor package, consisting of MEG and another commercial corrosion inhibitor. Some of the synthetic gasolines were also additised with a commercial detergent for detergency testing.

For comparison purposes, a RON 95 crude-derived fuel was obtained. The following fuels were selected for analysis:

1. R95 crude-derived fuel, (RON 97, MON 86). The fuel was a commercial base fuel containing no performance additives.
2. R95 crude-derived base fuel containing 10% bio-ethanol
3. R95 crude-derived base fuel containing 10% SFA
4. R95 crude-derived base fuel containing 10% Sasol 99% synthetic ethanol

The crude-derived gasoline was similar in properties to the synthetic gasoline. It had a RON of 97.2 and a MON of 86.1. The alcohol-containing blends had higher FVI and Reid Vapour Pressure (RVP) values.

These fuels were used (in additised and unadditised form) in the wet and dry corrosion evaluations. Additionally, for the wet corrosion work, 2% blends were also prepared in order to investigate the wet corrosion influence of lower percentages of ethanol as there had been concerns with the wet corrosion properties of alcohol-containing fuels at lower ethanol contents.

6.1.2 Ethanol used in the detergency and IVD evaluation work

A 99% pure sugar derived bio-ethanol was obtained from Illovo, South Africa.

Synthetic Ethanol Lights is 99% pure and is generally sold for non-automotive applications, has a purity level similar to that of bio-ethanol. A SFA sample (95% pure) was used in the comparison. The major components in the three alcohols are given in Table 2:
Table 2: Composition of the bio-ethanol, ethanol lights and SFA used in this Study

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sasol Fuel Alcohol (SFA)</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>94.94</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>1.41</td>
</tr>
<tr>
<td>Di-ethyl ether</td>
<td>0.37</td>
</tr>
<tr>
<td>1-ethoxy propane</td>
<td>0.50</td>
</tr>
<tr>
<td>1-Methyl ethyl acetate</td>
<td>0.91</td>
</tr>
<tr>
<td>1-Ethoxy butane</td>
<td>0.39</td>
</tr>
<tr>
<td>Bio-ethanol</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>99.99</td>
</tr>
<tr>
<td>Unknown</td>
<td>0.002</td>
</tr>
<tr>
<td>Ethanol Lights</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>99.94</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>0.01</td>
</tr>
<tr>
<td>Ethyl acetate + hexane</td>
<td>0.02</td>
</tr>
<tr>
<td>2,4-dimethyl-1,3-dioxane</td>
<td>0.02</td>
</tr>
<tr>
<td>Unknown</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Several other components form part of the typical composition of SFA. This includes iso-propanol which, at 1.41% is the component in the SFA at the second highest concentration. Diethyl ether and 1-methylethyl acetate were also major components detected in the SFA. The bio-ethanol was of very high purity. The ethanol lights were 99.94% pure. All blends were prepared by laboratory scale blending.

6.2 Inlet valve deposit testing (IVD testing)

For this study, the IVD tests were performed according to an in-house developed test method that is similar to the Coordinating European Council (CEC) test method (CEC F-05-93). These test methods are designed to evaluate the propensity of gasoline or gasoline additive formulations to prevent intake valve deposits in fuel injected engines [23].

The Briggs & Stratton (B&S) single cylinder IVD test was originally set up by Sasol to provide a cost effective alternative IVD test to the CEC F-05-93 test which is both expensive and time consuming. The idea was to use the B&S test as a screening test, especially in cases where a large number of fuel and/or additive combinations needed to be tested. From the B&S results the most critical or suitable fuel blends or fuel/additive combinations could be selected for further testing.

Currently the B&S test is still used for screening purposes, but at times it is also used for more fundamental type research projects where new or exotic fuel blends have to be tested.

6.2.1 Engine and Hardware

The test bench essentially consists of a Briggs & Stratton Vanguard single cylinder industrial engine that is connected to an electric generator. The generator is loaded by a 3 kW oil filled fin heater. Table 3 below gives the engine specifications.

Table 3: Engine specifications of the engine used for IVD testing

<table>
<thead>
<tr>
<th>Description</th>
<th>B&amp;S Vanguard single cylinder 4-stroke</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model number</td>
<td>130000-38432</td>
</tr>
<tr>
<td>Displacement</td>
<td>216 cm$^3$</td>
</tr>
<tr>
<td>Bore</td>
<td>72.0mm</td>
</tr>
<tr>
<td>Stroke</td>
<td>53.0mm</td>
</tr>
<tr>
<td>Power output</td>
<td>5.6kW (7.5HP)</td>
</tr>
<tr>
<td>Engine cooling</td>
<td>Air cooled</td>
</tr>
<tr>
<td>Fuel supply</td>
<td>Carburettor</td>
</tr>
</tbody>
</table>

6.2.2 Test Operation

During preparation for each test, a new inlet valve is weighed and then fitted to the engine. Before the test is started, the engine is warmed up by running it at idle speed under no load conditions for 3 minutes. Thereafter the test is started and the engine runs for 6 hours in a dual-stage duty cycle consisting of 30 seconds idle (no load) followed by 90 seconds under approximately 50% load at 3000 rpm. The load switching is done by a pneumatic actuator that opens the throttle and the load is then regulated by the engine's built-in mechanical regulator according to the engine speed. The electric load is automatically switched off when the throttle is closed.

Fueling is handled by the standard fuel system (5L
on-board fuel tank feeding a single choke carburettor) and the engine is stopped twice during the 6 hours for refuelling.

After each test, the engine is disassembled and the inlet valve is removed and weighed again. The difference in weight between the "before" and "after" weight measurements is calculated and represents the weight of deposits that formed on the valve during the test.

Table 4 below provides a summary of the engine operating conditions.

Table 4: Engine operating conditions used for the single cylinder IVD screening tests

<table>
<thead>
<tr>
<th>Engine speed (Stage 1 &amp; 2)</th>
<th>Idle (800-1000 rpm) &amp; 3000 rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stage 2 load (% of Max)</td>
<td>~50%</td>
</tr>
<tr>
<td>Test duration</td>
<td>6 hours</td>
</tr>
<tr>
<td>Stage duration</td>
<td></td>
</tr>
<tr>
<td>Stage 1 (idle)</td>
<td>30 sec</td>
</tr>
<tr>
<td>Stage 2 (50% load)</td>
<td>90 sec</td>
</tr>
<tr>
<td>Temperatures</td>
<td></td>
</tr>
<tr>
<td>Oil</td>
<td>80 – 95 °C (monitored)</td>
</tr>
<tr>
<td>Exhaust gas</td>
<td>650 – 690 °C (monitored)</td>
</tr>
<tr>
<td>Inlet air</td>
<td>Ambient (not controlled/monitored)</td>
</tr>
<tr>
<td>Fuel</td>
<td>Ambient (not controlled/monitored)</td>
</tr>
<tr>
<td>Fuel consumption</td>
<td>9 – 10 litres</td>
</tr>
</tbody>
</table>

6.3 Wet corrosion testing

Wet corrosion testing was carried out according to ASTM D665, as discussed in Section 5.5.

6.4 Dry corrosion testing

Dry corrosion testing was carried out according to Section 5.3.

7. RESULTS: Comparison of the corrosion and IVD behaviour of synthetic petrol with bio-ethanol and synthetic ethanol blends respectively

7.1 Wet corrosion results: gasoline with 2% ethanol (synthetic and bio-ethanol)

Previous experience indicated that blends containing lower concentrations of ethanol may be more prone to wet corrosion than blends containing higher concentrations of ethanol, when blended into an unadditised base fuel. For this purpose therefore, 2% and 10% blends were assessed, as this was in line with Sasol's previous experience with synthetic ethanol. Blends of the synthetic gasoline base and bio-ethanol, synthetic lights and SFA respectively, were carried out in the laboratory. A similar blend matrix was evaluated for the crude derived base fuel. The results of the 2% ethanol addition on the wet corrosion (bio-ethanol and synthetic ethanol) are given in Table 5.

Table 5: Wet corrosion performance of 2% ethanol/gasoline mixtures

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Wet corrosion in synthetic base</th>
<th>Wet corrosion in crude derived base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base gasoline (unadditised)</td>
<td>Corrosive*</td>
<td>Corrosive*</td>
</tr>
<tr>
<td>Gasoline +2% bio-ethanol unadditised</td>
<td>Corrosive</td>
<td>Corrosive</td>
</tr>
<tr>
<td>Gasoline +2% bio-ethanol additised</td>
<td>Not corrosive</td>
<td>Not corrosive</td>
</tr>
<tr>
<td>Gasoline +2% SFA unadditised</td>
<td>Corrosive-slight</td>
<td>Corrosive</td>
</tr>
<tr>
<td>Gasoline +2% SFA additised</td>
<td>Not corrosive</td>
<td>Not corrosive</td>
</tr>
<tr>
<td>Gasoline +2% ethanol lights unadditised</td>
<td>Corrosive</td>
<td>Corrosive</td>
</tr>
<tr>
<td>Gasoline +2% ethanol lights additised</td>
<td>Not corrosive</td>
<td>Not corrosive</td>
</tr>
</tbody>
</table>

* expected for fuels containing no corrosion inhibitors

The unadditised laboratory blended synthetic base fuel was corrosive, as determined by wet corrosion testing. At 2% ethanol addition (bio-ethanol as well as synthetic alcohol) the unadditised ethanol-containing fuels were also equally corrosive. With the addition of the standard corrosion inhibitor package, no corrosion is observed with the package and corrosion is therefore successfully controlled.

The crude-derived base fuel also resulted in wet corrosion. At 2% ethanol addition, all the unadditised ethanol-containing samples were also corrosive. Similar to the synthetic base fuel results, the additised samples all passed the wet corrosion test. The bio-ethanol containing sample appeared to be slightly more corrosive than the ethanol lights-containing sample.
7.2 Wet corrosion results: gasoline with 10% ethanol (synthetic and bio-ethanol)

The 10% blends were evaluated under the same experimental conditions as the 2% blends. An example of the visual results is given in Figure 4. The wet corrosion properties of the 10% ethanol blends (in both the laboratory blended synthetic gasoline and the crude-derived coastal fuel) are given in Table 6.

At 10% ethanol addition into a synthetic base gasoline, both the 10% bio-ethanol and 10% synthetic alcohol-containing fuels (SFA and ethanol lights) were non-corrosive in the wet corrosion test. Blends containing 10% ethanol did not require corrosion additives to prevent wet corrosion. However, the use of additives is still recommended as a precautionary measure, due to possible dilution effects in the fuel logistical chain. These results are in line with previous experience by Sasol on ethanol-containing blends. Fuels containing relatively pure ethanol at 10% level have been proven over time to display less corrosion to mild steel even without the additives. Currently, the reasons for this are not fully understood and will be investigated further in future work.

Similar results were also noticed for the crude-derived coastal fuel, where the base fuel itself (no ethanol/additives added) was corrosive, while the ethanol-containing blends (additised and unadditised) resulted in no wet corrosion.

At 10% ethanol addition, the wet corrosion behaviour of the three alcohols was therefore shown to be comparable. The corrosion behaviour of the crude-derived base gasoline was also comparable to the synthetic base gasoline, indicating no concern with regards to ensuring a non-corrosive fuel in the market.

7.2.1 Dynamic alcohol corrosion testing: 2% Synthetic gasoline/ethanol blends

Initial DAC testing was carried out on 2% levels of SFA and ethanol lights in the synthetic base fuel, in comparison with a 2% bio-ethanol containing sample. No corrosion problems were noticed. Samples containing 1:1 blends of ethanol lights and SFA (at 2% total addition) were also investigated, and similar to the bio-ethanol, ethanol lights and SFA, blended individually into the synthetic gasoline base, no corrosion was noticed. This seems to be in contrast with the results obtained previously [4]. However, these fuels were leaded fuel blends, which were more corrosive.

Additised and unadditised samples also performed comparably. In general, the synthetic ethanol containing samples (additised and unadditised) performed similarly to the bio-ethanol containing samples (additised and unadditised).

7.2.2 Dynamic alcohol corrosion testing: 10% Synthetic gasoline/ethanol and 10% crude-derived blends

Higher levels of alcohol in a fuel are expected to be more severe with regards to dry corrosion, in comparison to wet corrosion, where typical experience indicates that the lower alcohol levels may potentially
be more corrosive. In order to study the effect of higher alcohol levels, dry corrosion testing was also carried out on 10% ethanol blends, using both synthetic ethanol and bio-ethanol. An example of the experimental outcome is given in Figure 5, where the comparative unadditised and additised 10% bio-ethanol and Ethanol lights samples are compared. The qualitative results are given in Table 7.

![Figure 5: Dry corrosion results of the 10% bio-ethanol and 10% ethanol lights containing samples in a synthetic base](image)

**Table 7: Dry corrosion properties of the 10% fuel blends evaluated in this study**

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Dry corrosion in synthetic base fuel</th>
<th>Dry corrosion in crude derived base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base gasoline fuel (unadditised)</td>
<td>Not corrosive</td>
<td>Not corrosive</td>
</tr>
<tr>
<td>Gasoline +10% bio-ethanol unadditised</td>
<td>Slight corrosion</td>
<td>Not corrosive</td>
</tr>
<tr>
<td>Gasoline +10% bio-ethanol additised</td>
<td>Not corrosive</td>
<td>Not corrosive</td>
</tr>
<tr>
<td>Gasoline +10% SFA unadditised</td>
<td>Not corrosive</td>
<td>Slight corrosion</td>
</tr>
<tr>
<td>Gasoline +10% SFA additised</td>
<td>Not corrosive</td>
<td>Not corrosive</td>
</tr>
<tr>
<td>Gasoline +10% ethanol lights unadditised</td>
<td>Slight corrosion</td>
<td>Not corrosive</td>
</tr>
<tr>
<td>Gasoline +10% ethanol lights additised</td>
<td>Not corrosive</td>
<td>Not corrosive</td>
</tr>
</tbody>
</table>

None of the additised synthetic fuel blends containing alcohol (synthetic and bio-ethanol) resulted in any dry corrosion. Some of the unadditised ethanol-containing blends did however result in corrosion when not additised with the corrosion inhibitor package. The commercial corrosion inhibitor package therefore, was successful in controlling corrosion of these fuels.

With the crude-derived fuels, the unadditised bio-ethanol containing sample resulted in some dry corrosion, limited to small spots on the specimens. No corrosion was however, noticed on the sample, exposed to the head space vapours in the reactor. The 99% synthetic ethanol and SFA containing samples were not corrosive. Overall the dry corrosion behaviour of the crude derived and synthetic fuel blends were comparable.

### 7.3 Inlet valve deposit testing

The results of the inlet valve deposit tests, determined as per the experimental procedure given in Section 6.2, are given in Figure 6.

![Figure 6: B&S IVD results of the fuels evaluated in this study](image)

From the results presented in Figure 6, it can be seen that all the unadditised fuels performed similarly in the tests. A thorough statistical analysis was performed on the results and showed that none of the measured differences in IVD mass are statistically significant at the 95% confidence interval. This suggests that neither synthetically produced ethanol (ethanol lights) nor bio-ethanol adversely affected the IVD mass in the tests carried out. The results appear to be in slight contrast with the general consensus that a 10% ethanol blend would result in a moderate increase in IVDs [24]. However, given that the testing was carried out on a single cylinder engine, the sensitivity of the test may be slightly lower than the industry accepted M102 tests.
The three results for the additised fuels showed that a standard level of DCA is effective in keeping the inlet valve clean.

From the results presented in the previous section it is clear that neither synthetically produced ethanol nor bio-ethanol adversely affect IVD formation in this specific application. Also, the standard DCA treatment is sufficient for controlling IVD formation in the fuels tested.

8. Conclusions

In this article, an overview is given of the historic experience of Sasol with the incorporation of SFA into the South African fuel pool. Factors that need to be taken into consideration include blending, logistical factors as well as performance in end-use applications. Transport of ethanol mixtures through a pipeline network also presents problems, which were successfully overcome by Sasol. Due to initial problems with corrosion, Sasol’s synthetic fuel alcohol has changed in composition in order to reduce the amount of heavy alcohols. This resulted in a decrease in the corrosion propensity of the resulting alcohol mixture.

The availability of bio-ethanol may increase in South Africa and it is therefore important to understand the behaviour in blends. Given Sasol’s experience with synthetic ethanol in the South African market, similar testing and additisation was applied to bio-ethanol/gasoline blends and tested for dry and wet corrosion. This testing is important in ensuring that current additive packages are sufficient to problem-free use of bio-ethanol in the South African fuel pool.

In this study, the effect of bio-ethanol was contrasted with synthetic alcohols, in both synthetic gasoline and crude-derived matrices, with regards to wet and dry corrosion testing. Dry corrosion testing was carried out using Sasol’s in-house mini dynamic alcohol corrosion apparatus. Generally the dry corrosion properties of the bio-ethanol blends (at 10% in synthetic and crude-derived gasoline) were comparable to that of both a Sasol fuel alcohol and a 99% pure ethanol lights sample. Although some of the laboratory prepared base fuels were corrosive, the additive package currently used for synthetic ethanol could be transferred to the bio-ethanol containing gasoline, resulting in no further corrosion.

Both the base gasolines and the ethanol containing fuels (at 2% ethanol content) were corrosive during the wet corrosion test. These fuels required additisation in order to prevent wet corrosion. At 10% ethanol (bio-ethanol and synthetic ethanol) none of the fuels were corrosive in the wet corrosion test. However, as a precautionary measure, it is recommended to additise these fuels to prevent deviations in the marketplace.

Single cylinder IVD screening tests indicated small differences between the base fuel and the alcohol containing base fuels for the synthetic base gasoline fuel matrix. For the synthetic gasoline, additisation with a commercial detergent package reduced the level of deposits to similar low levels. No differences were found between the additised alcohol containing samples, within the sensitivity of the method used. The sensitivity of the technique however, was not yet benchmarked against the M102 test. It is however, important to note that these conclusions are relative to the purity of ethanol and may change as the level or type of contamination changes.

The dry and wet corrosion properties of bio-ethanol/synthetic gasoline were generally shown to be comparable to that of a synthetic ethanol/synthetic gasoline matrix, with only slight differences noticed.

A major challenge will be to ensure that the bio-ethanol, supplied for blending with any crude-derived or synthetic base fuel, complies with strict fuel ethanol specifications applicable to the region, as it may significantly alter the corrosion and possibly detergency properties of the fuels.

References:


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[14] Sasol internal report


[18] Sung, R. L., US patent 4,376,635, *Novel gasohol or ethanol composition containing as a corrosion inhibitor the reaction products of benzothiazole, formaldehyde and an n-alkyl propylene diamine*. 1983


