

Effects of Fuel Impurities and Additive Interactions on the Formation of Internal Diesel Injector Deposits

Jörg Ullmann, Marion Geduldig, Robert Bosch GmbH, Corporate Sector Research and Advance Engineering, CR/ARA, Germany

Heinz Stutzenberger, Robert Bosch GmbH, Diesel Systems, DS/ENF, Germany

Rinaldo Caprotti, Graham Balfour, Infineum UK

Dennis Hess, Infineum USA, LP

SUMMARY

The development of high performance high pressure diesel fuel injection systems has significantly improved efficiency, driving performance and at the same time substantially reduced emissions of diesel engines. Today's diesel injection systems are operated at pressures of up to 2000 bar, with typical injection quantities ranging from 1 mm³ at pilot injection up to 40 mm³ during full load for passenger car applications. Moreover, injection times of 1 to 2 milliseconds and multiple injection strategies will result in up to 10,000 injections per minute. Considering the performance requirements and the small clearances required for high pressure fuel injection systems, for example a 1 µm plunger clearance inside the injector, any internal deposit can adversely impact the precision of the injection and vehicle operability over its lifetime.

In this paper, the occurrence and effects of fuel deposits are reported and investigations into their formation are discussed. Three different types of deposits have been identified: polymeric organic material with specific additive related structural elements, fuel oxidation products and sodium ion containing compounds like sodium fatty acid soaps and sodium chloride. These deposits are found inside the fuel injection system at various places depending on their nature and pathway of formation.

For each category of deposits, the analytical evidence is given on how the deposits have been identified. The analytical techniques applied include Gel Permeation Chromatography (GPC), Fourier Transform Infra Red (FTIR) spectroscopy, Scanning Electron Microscopy (SEM) and elemental analyses by X-ray fluorescence (EDS). If the physical and chemical analysis results did not allow for full clarification of the deposit material, additional laboratory experiments were performed. This has been especially helpful for understanding how metal ion impurities, mono-/di-fatty acids and detergents of the polyisobutylene succinimide (PIBSI) type can contribute to deposit formation. From this understanding an approach is proposed regarding how to avoid, as much as possible, the formation of such type of deposits.

1 INTRODUCTION

Diesel injector deposits are mainly associated with nozzle coking. Deposits inside sprayholes are known to reduce the flow of the fuel, those on the nozzle tip can lead to a distortion of the optimum spray pattern if they project over the opening of the sprayhole. Improved nozzle design, progress in fuel cleanliness and the use of effective additives have contributed to reduce the degree of nozzle coking. Today, nozzle coking is still an issue, if fuel quality is poor and fuels contain metallic impurities like zinc or sodium or organic high molecular impurities, e.g. triglycerides deriving from admixed biofuels.

In this paper, however, the focus is on internal injector deposits that are found further inside the injector body, e.g. at the armature group, on the piston

and nozzle needle and inside the nozzle body. The deposits adversely affect the injector dynamics, having an influence on the injection precision, mainly on the injection amount and timing. The effects resulting from internal deposits can be varied depending on their position and extension inside the fuel system. At short injection times, e.g. during pilot injection, the injection amount typically being as low as 1 mm³ in passenger car applications, can be doubled since the deposits affect the opening and closing of the needle differently. Whereas the opening of the injector is determined by the prevalent injection pressure, the closing is delayed by a slowdown of the injector performance. Although small amounts of deposits are tolerated by the injectors, and their adverse effects can be

compensated e.g. by self re-adjusting functions, an increasing number of complaints are being reported. Generally, the deposits are recognised by their adverse effects on driveability. Some vehicles have also shown severe operability problems like rough running engines. Internal deposits can also impact the injection system by strong power loss, which has been experienced when their deposition was concentrated inside the nozzle body in the area of the needle seat.

The deposits identified here have been encountered sporadically, but also locally and periodically to a significant extent. The deposition of sodium fatty acids soaps, for example, has been reoccurring repeatedly, showing that there is a constant risk although their formation pathway is quite well understood. This paper is intended to show that the deposits hitherto identified have already been responsible for serious performance problems. It can also not be excluded that these might expand to significant field problems if no appropriate measures are taken for their prevention.

Additionally, fuel quality is changing worldwide. Desulphurisation and biofuel blending account for a reduction in oxidation stability and new sources of impurities. Both exacerbate the deposit forming tendency. Modern enhanced fuel injection equipment, developed for Euro V emission standards, impose additional performance requirements on the fuel. Reducing emissions further requires the use of sophisticated injection patterns with multiple injections per injection cycle to increase the injection pressure to 2000 bar and higher. The clearance between the moving parts is being reduced further and so the same amount of fuel deposit will have an even greater effect. Also, from this perspective, the risk for negative impacts is increasing. Therefore, it is advisable to proactively take measures in order to avoid fuel deposits in the future, that are already present today.

In this paper, major deposit formation pathways are discussed. Based on this understanding, approaches are recommended to control these potential issues.

2 DEPOSIT CLASSIFICATION

Summarising the results of chemical deposit analyses from various injectors with technical issues suggests a classification into three different categories:

1. Polymeric organic material with additive related constituents
2. Fuel oxidation products
3. Sodium containing compounds
 - a. Sodium soaps
 - b. Sodium chloride

3 POLYMERIC ORGANIC MATERIAL WITH ADDITIVE RELATED CONSTITUENTS

In a recent publication [1] the analytical evidence for the composition of this special kind of polymeric material was described. This is found inside the injectors, particularly at the armature group, on the hydraulic plunger and nozzle needle.



Figure 1: Armature plate, valve piston and nozzle needle with deposits consisting of polymeric organic material with additive related constituents. The scratches derive from a needle used to remove material for analysis.

The deposit (figure 1), often brownish and sticky, is insoluble in all typical laboratory solvents or mixtures thereof that makes its full characterisation difficult. Investigating the solids obtained from the field and from engine testing with FTIR always yielded very similar fingerprints, confirming that the deposits are not a varying mixture of different components.

In figure 2 the FTIR spectra of the two typical polymeric deposits A and B are given. The IR traces are assigned to a polymeric reaction product of detergents of the polyisobutylene succinimide class with acidic fuel components. Generally, the deposit spectra reveals characteristic absorptions at

- 3305 cm^{-1} , assigned to an amino group (N-H)
- 1660 and 1555 cm^{-1} , representing amide bondings
- 1471, 1390, 1366 and 1231 cm^{-1} (type A) and 1471, 1389, 1377, 1366 and 1231 cm^{-1} (type B), indicating the presence of isobutylene groups.

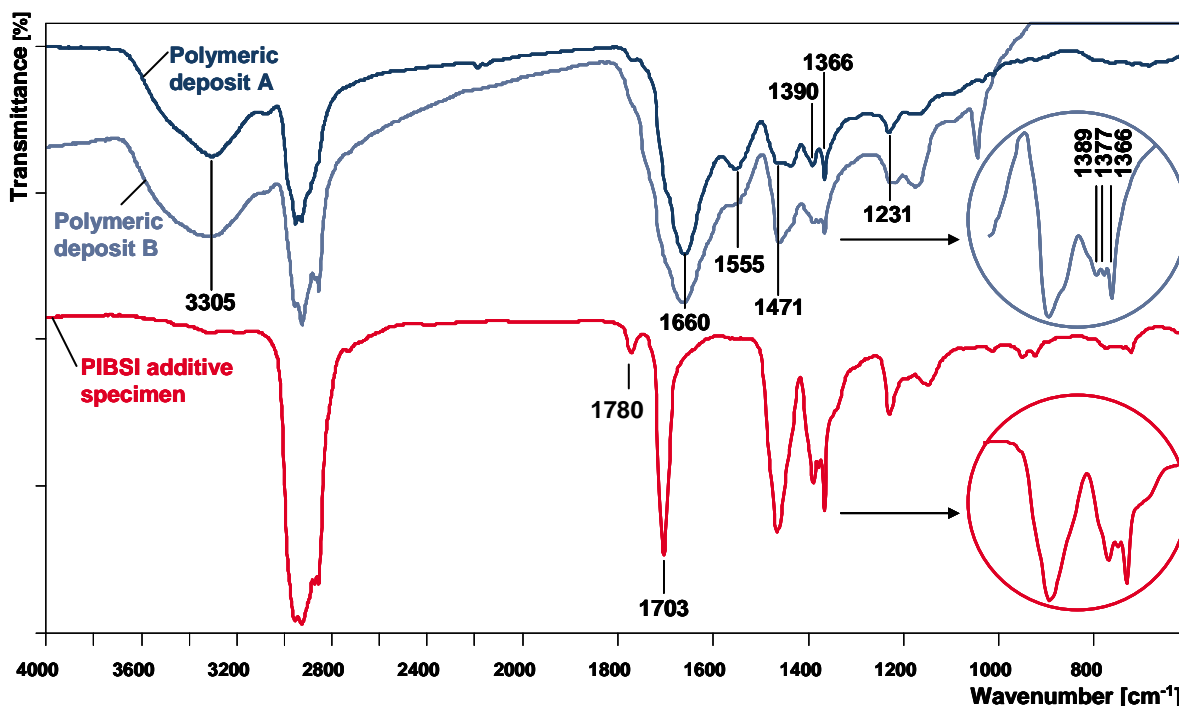


Figure 2: FT Infrared spectra of the polymeric material with additive related constituent

For comparison, a spectrum of a PIBSI additive specimen is displayed (bottom line in figure 2), showing succinimide vibrations at 1703 and 1780 cm^{-1} and the same isobutylene pattern as found in deposit B.

PIBSI additives are widely applied in diesel fuel and are expected to be ubiquitous in the fuel system. Wetting of surfaces with PIBSI, however, occurs in very thin films that are far beyond the detection limit of the FTIR method. Owing to the sensitivity limitations of the FTIR method, the PIBSI detergent itself never appears in the FTIR spectra of injection system deposits.

Owing to the restrictions imposed on the analysis of the polymeric deposit material by its insolubility, specific laboratory experiments with PIBSI specimens were carried out in order to further elucidate the structure of the deposits and to understand the formation route.

The focus of the experimental work is on the reactivity of PIBSI additives with acidic fuel components, primarily with mono- and di-fatty acids, used respectively as lubricity improvers or corrosion inhibitors and with formic acid. Traces of formic acid are omnipresent in fuels and its concentration grows exponentially after fuel ageing has started.

3.1 LABORATORY TESTS

3.1.1 TEST CONDITIONS

The test components were a commercially available detergent of the PIBSI type, mono- and di-fatty acids and reagent grade formic acid. In some experiments an industrial polyamine was also added in order to cover the influence of other amine-based additives or even of polyamines themselves that can be a residue in industrial grade PIBSI detergents, even though at very low concentrations.

The components were reacted without dissolving them in fuel in order to facilitate the IR analyses of the reaction products. Methylene chloride and heptane were used for the work-up of the reaction mixture that was then identified by FTIR and GPC techniques.

The reaction temperature, time and the material ratios used are given below. None of the components underwent any meaningful change if treated individually under the applied conditions.

3.1.2 RESULTS WITH PIBSI AND DI-FATTY ACIDS

2.13 g PIBSI and 0.6 g di-fatty acids were treated at 180 $^{\circ}\text{C}$ for 16 hours. After the work-up, the reaction product showed broad additional peptide bondings in the FTIR spectrum. The typical FTIR trace of the di-fatty acid disappeared (figure 3).

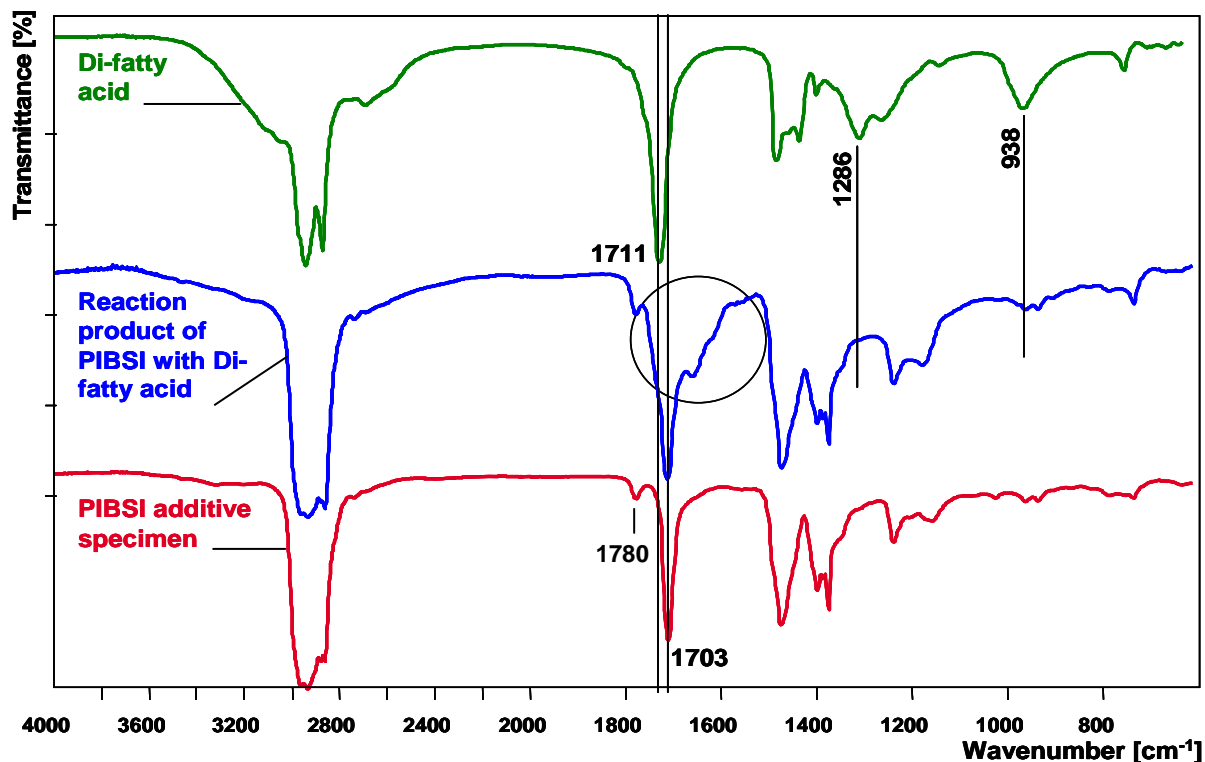


Figure 3: FT Infrared spectra of the reaction product formed from PIBSI and di-fatty acids

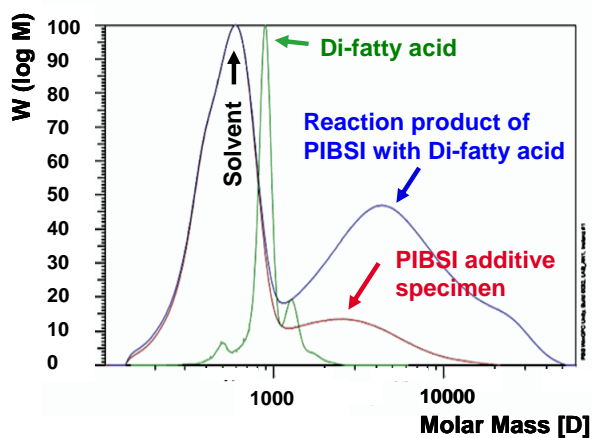


Figure 4: GPC of the reaction product formed from PIBSI and di-fatty acids

The GPC trace confirms the reaction: the reaction product does not show a visible peak of the di-fatty acid. Instead, the average molecular mass distribution is increased compared to the PIBSI detergent (figure 4).

For the reference GPC the PIBSI specimen was taken directly, not as a mixture with di-fatty acid. Since the weight ratio of the starting materials PIBSI and di-fatty acid is 3.5 : 1, the conversion rate is actually 30 percent higher than suggested when comparing the graphs of PIBSI and the reaction product.

3.1.3 RESULTS WITH PIBSI AND FORMIC ACID

0.62 g PIBSI and 2 ml formic acid and 0.14 g polyamine were reacted at 120 °C for 19 hours. The FTIR spectrum of the conversion product displayed almost the same fingerprint as the polymeric deposit material found in the injectors (figure 5).

The reaction of PIBSI with formic acid and polyamine is confirmed by the GPC displayed in figure 6. The transformation product again showed an increase in the molecular weight. Although the graphs indicate a medium conversion rate only, the turnover is in fact quite high. The PIBSI specimen was taken directly again for the purpose of recording the GPC reference trace but consisted of 22 % mass only in the starting material of the experiment.

For comparison, formic acid (2 ml) and polyamine (0.08 g) were treated under the same conditions without PIBSI.

The product formed from formic acid and polyamine displayed a low molecular weight distribution in the GPC as expected, giving evidence once more that the polymeric material is only formed in the presence of the PIBSI additive. The characteristic isobutylene vibrations found in the FTIR spectra of the injector deposits clearly indicate the involvement of PIBSI.

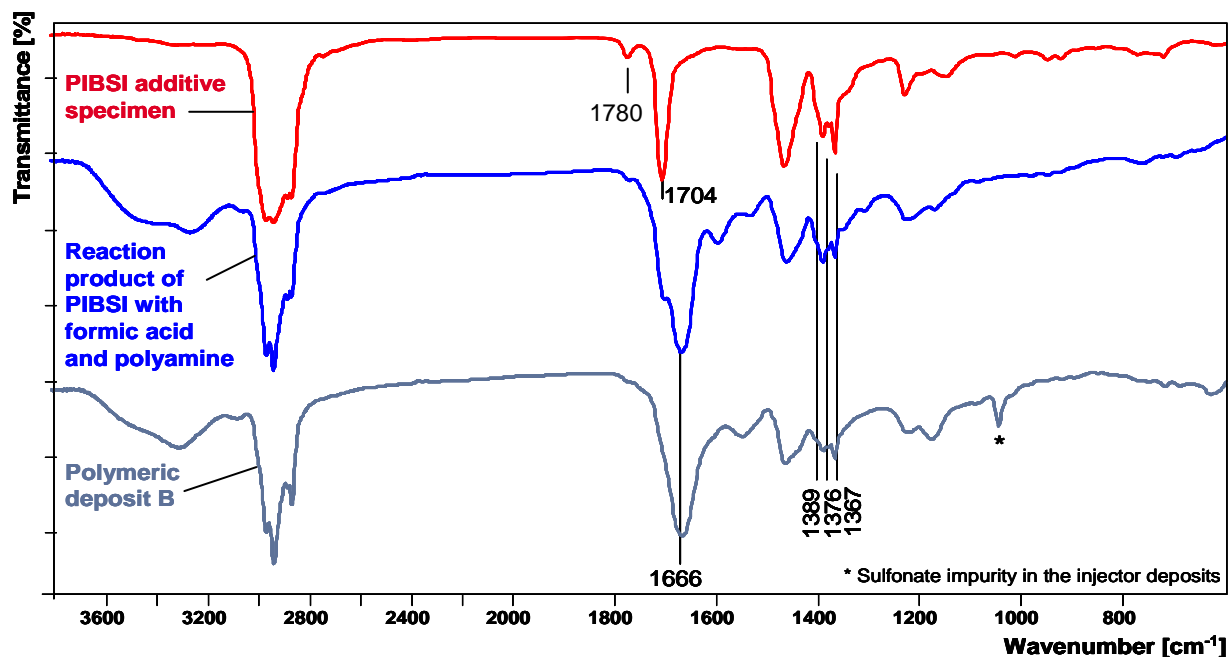


Figure 5: FT Infrared spectra of the reaction product formed from PIBSI, formic acid and polyamine

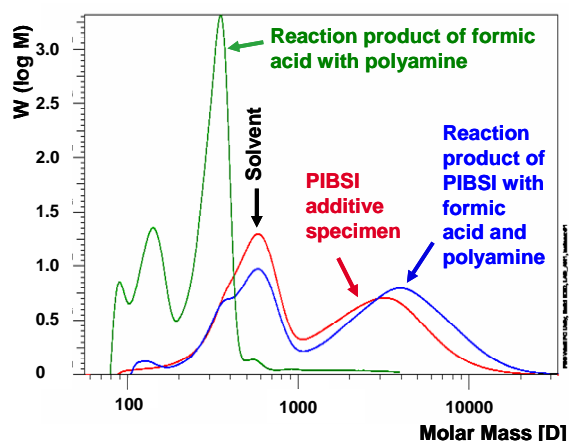


Figure 6: GPC of the reaction product formed from PIBSI, formic acid and polyamine.

The occurrence of polymeric deposits with additive related constituents can be restricted or even avoided if

- acidic additives are replaced by neutral chemistries, e.g. ester based lubricity additives
- fuel stability is increased to a level that prevents fuels from forming formic acid and their higher molecular weight homologues prior to its full consumption, and
- additional attention is paid to the chemical reactivity of additives in fuels, in order to minimise the possibility that their functional groups react to form insoluble material.

3.1.4 CONCLUSION FROM THE EXPERIMENTS

Both conventional PIBSI detergents and acidic components like fatty acids or formic acid are prevalent in a standard fuel environment. Laboratory tests showed that reacting these components yields products similar to the sticky deposit-like material found in the injectors. In the laboratory experiments the reaction of additives with acids is certainly facilitated by their high concentration. The formation of deposits in the injectors might be supported in a similar way by the metallic surfaces where the polar components are brought together by adsorption.

4 FUEL OXIDATION PRODUCTS

In fuel markets with high and well controlled stability levels, incidents by aged fuel are only encountered in borderline applications and during longer immobilisation periods. The future European EN 590 update due in 2009, now includes the oxidation stability parameter “Induction period” (EN 15751) with a minimum stability limit of 20 hours. This is considered as a milestone for vehicle protection. If common rail injectors are operated with fuels of poor stability, or even with fuels that already contain aged components, the polymeric material is deposited at the armature/magnet (figure 7).

Polymers and acids from ageing also have distinctive FTIR spectra, displayed in figure 8. The appearance of the FTIR fingerprint largely depends on the condition of the fuel oxidation products.

Partly burned hydrocarbons, e.g. in deposits at the nozzle tip, show broad carbonyl vibrations at 1723 and 1604 cm^{-1} , indicating that the molecular structure is destroyed to a large degree (8a).

Fuel ageing products show more pronounced fingerprints. The shape depends on the fuel source (diesel or fatty acid methyl ester, FAME).

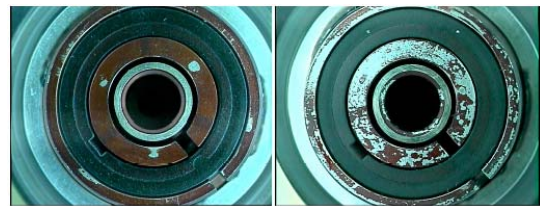


Figure 7: Armature/magnet of a heavy-duty common rail injector with polymers

left : directly after dismantling
right: after incomplete clean-up

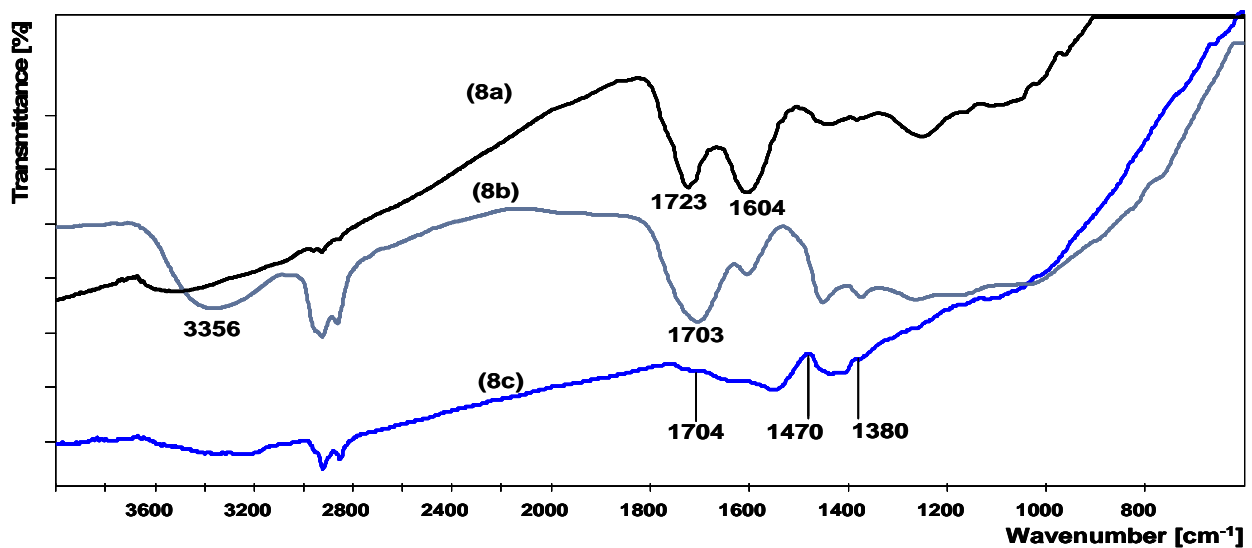


Figure 8: FT Infrared spectra of diesel fuel oxidation products

(8a) Partly burned hydrocarbons (8b) Diesel ageing product (8c) Soaps of fuel ageing acids

Diesel ageing products show strong signals for the ageing acids (1703 cm^{-1}) and hydroxide groups (3356 cm^{-1} , 8b). In metal ion contaminated fuels the ageing acids are captured and transformed to the respective soaps. Since fuel ageing provokes various ageing acids, the different carboxylic soap absorptions amount to two broad signals from 1704 to 1470 and 1470 to 1380 cm^{-1} (8c).

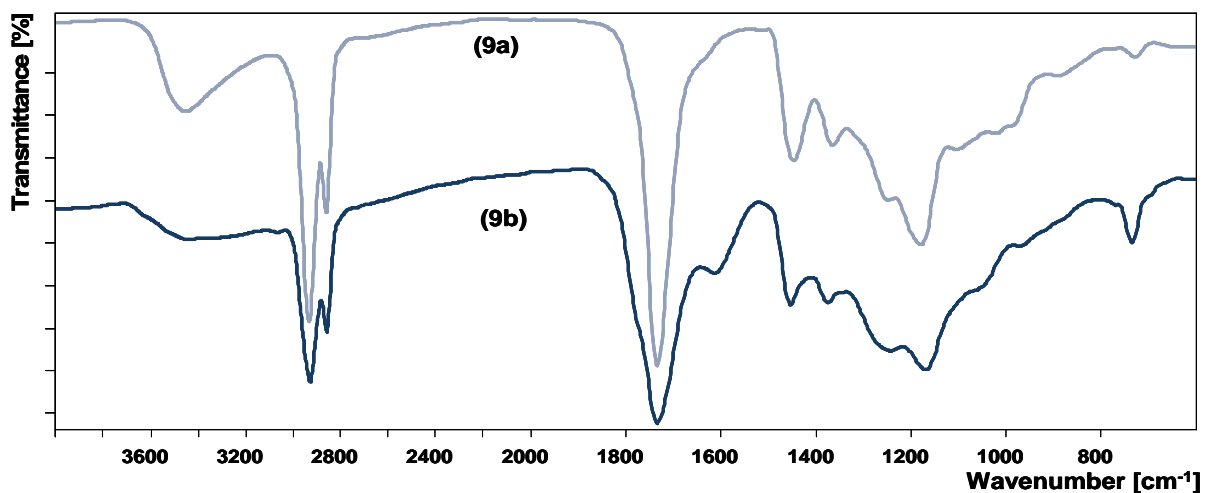


Figure 9: FT Infrared spectra of FAME oxidation products

(9a) Products of freshly aged FAME (9b) Products of aged FAME after post-curing

FAME ageing products are characterised by their ester vibration, that is broadened and shifted to lower wavenumbers (1734 cm^{-1}) compared to fresh FAME (1747 cm^{-1}). Figure 9 shows the IR traces of freshly aged FAME (9a) and aged FAME that was further thermally treated (9b), e.g. during its deposition inside the fuel injector. Since the spectra displayed stand for aged fatty acid esters in general, it can not be determined, whether the ageing products originate from FAME fuel or from fatty acid ester based lubricity additives used to improve lubricity in FAME-free diesel fuel.

5 SODIUM CONTAINING COMPOUNDS

Sodium deposits in the fuel equipment interfering with the injection performance can mainly be assigned to sodium soaps or sodium chloride. Clear proofs of their structure and solubility experiments with sodium salts give an idea how much sodium can be collected by the fuel and how these deposits are formed.

5.1 SODIUM SOAPS

Metal soap formation in fuel systems by the interaction of fatty acids with sodium contaminants was described recently [1]. This type of interaction was also reported from the incompatibility of fuel and oil additives [2, 3].

Metal soaps found as white material can easily be identified by their distinctive pattern of vibrations in the Fourier transform infrared (FTIR) spectrum that can be assigned to specific C18 fatty acid soaps (figure 10).

The fatty acid composition is deduced from gas chromatography after derivatisation with trimethylsulfonium hydroxide. The metal ion is often sodium that is evidenced by scanning electron microscopy and energy dispersive spectrometry (SEM/EDS).

Fatty acid based lubricity improvers undergo soaping, when sodium impurities are present in the fuel. Even trace concentrations of sodium near their analytical detection limit (0.1 mg/kg) can lead to the formation of sodium fatty acid soaps, as incidents with sodium contaminated fuels from pipelines have shown in the past. Soaps had a serious impact on the operability of vehicles by clogging fuel filters and by being deposited everywhere in the low and high pressure fuel circuit. Field injectors from Spain and the US show an increased occurrence of deposits consisting of sodium soaps. There are indications of improper housekeeping of the storage tanks and that the increasing use of biodiesel blends are further aggravating this situation.

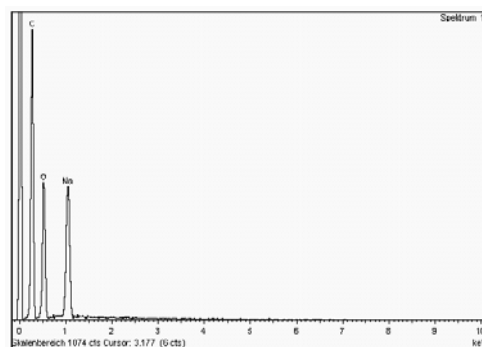
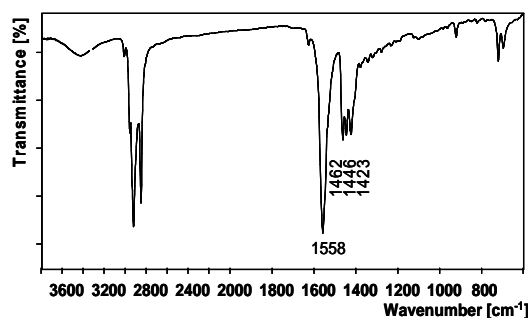


Figure 10: Nozzle needle with deposit of sodium fatty acid soaps: FTIR spectrum and SEM/EDS elemental analyses

Zinc soaps are also known to produce deposits, mainly inside the nozzle sprayholes and on top of the nozzle. This kind of deposit formation, that is influenced by high temperature and the combustion gas atmosphere, is part of nozzle coking. Nozzle deposits are not classified as internal injector deposits and hence are not described in this paper.

5.2 SODIUM CHLORIDE

Injector deposit analysis can reveal significant amounts of sodium chloride. Performance complaints have been seen in the US after ULSD operation and during engine tests in Europe with B5. Under unknown circumstances, sodium chloride separated from the fuel on the injector valve needle (figure 11) and inside the

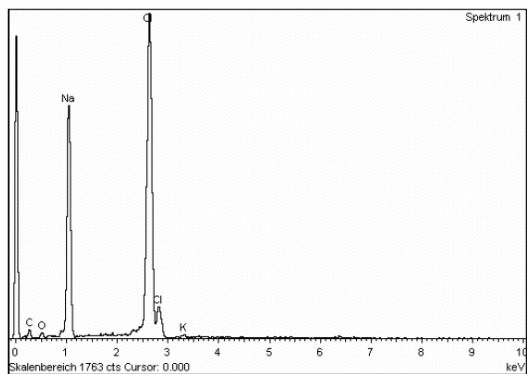
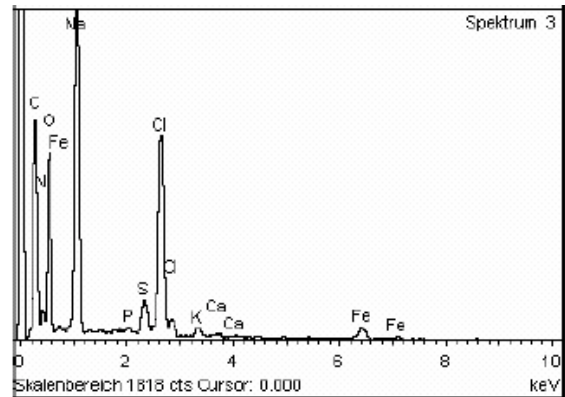
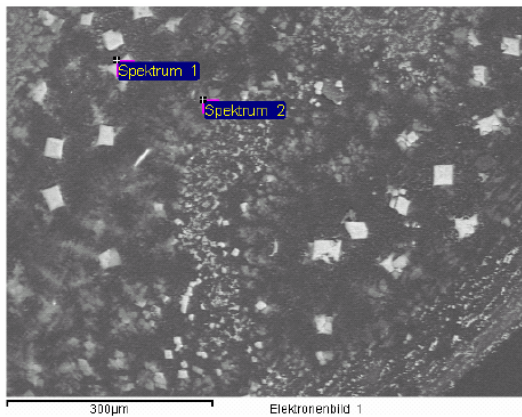
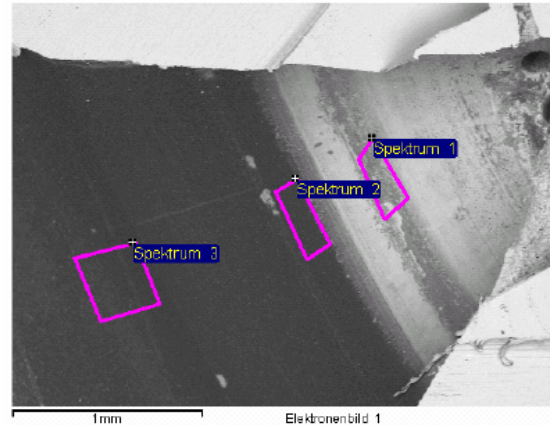
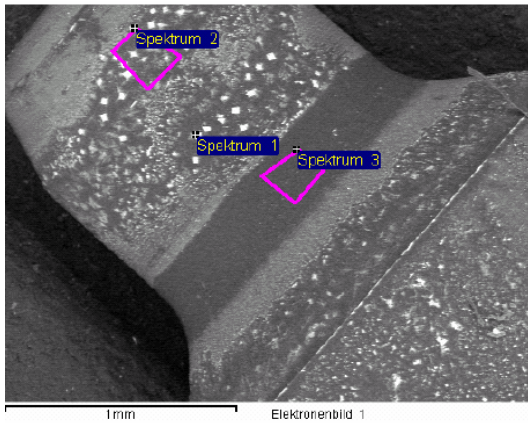


Figure 11: Injector valve needle with sodium chloride deposits: SEM/EDS elemental analyses

nozzle body just in front of the needle seat (figure 12).

One possible way of carrying over sodium is to use salt dryers that are used to finish “wet diesel” in refinery situations with insufficient time to coalesce and settle water. This is usually done using packed columns/vessels that contain sodium or calcium chloride. The hydration of the chloride salt is the mechanism that removes dissolved/ entrained water from diesel fuel.

In a side-reaction, acids can absorb sodium ions. Naphthenic acid, a trace component in diesel fuel, can react with the salt bed used for dewatering creating fuel soluble sodium naphthenate, the “carry-over” for sodium.

Figure 12: Nozzle body with sodium chloride deposits just in front of the needle seat: SEM/EDS elemental analyses

However, the sodium naphthenate can then exchange with non-neutral fuel additives like fatty acids finally leading to soap formation, visible by flocculation of suspended fine particles or the formation of a precipitate.

In further investigations, the interaction of sodium naphthenates with fatty acids and other lubricity additives was studied. Since little is known about the solubility of sodium chloride in diesel fuel, the uptake of sodium by fuels was also investigated in laboratory tests.

5.3 LABORATORY TESTS

5.3.1 TEST 1: INTERACTION OF SODIUM NAPHTHENATES WITH FATTY ACIDS AND OTHER LUBRICITY ADDITIVES AND THEIR INFLUENCE ON DEPOSIT FORMATION

5.3.1.1 TEST CONDITIONS

Diesel fuel (100 ml in cone-bottom centrifuge tube) was treated with 100 mg/kg of sodium naphthenate; this is equivalent to 12 ppm of sodium ions. This sodium concentration is about 3 to 4 times that in typical carry-over situations, and was purposely

increased to exacerbate potential interaction in this screening study. Then acid based, ester based and amide based lubricity additives were added to different samples/tubes, with treat rates adjusted to match the level of active ingredients. The fuel samples were then kept for five days at 40 °C, observed for sediment/floc formation and then centrifuged.

5.3.1.2 RESULTS

The sample treated with fatty acid based lubricity additive displayed a substantial level of visible suspended deposits ahead of the centrifuge step. The other samples containing ester or amide based lubricity additives did not visibly show any solids formation or separation even after centrifuging (figure 13).

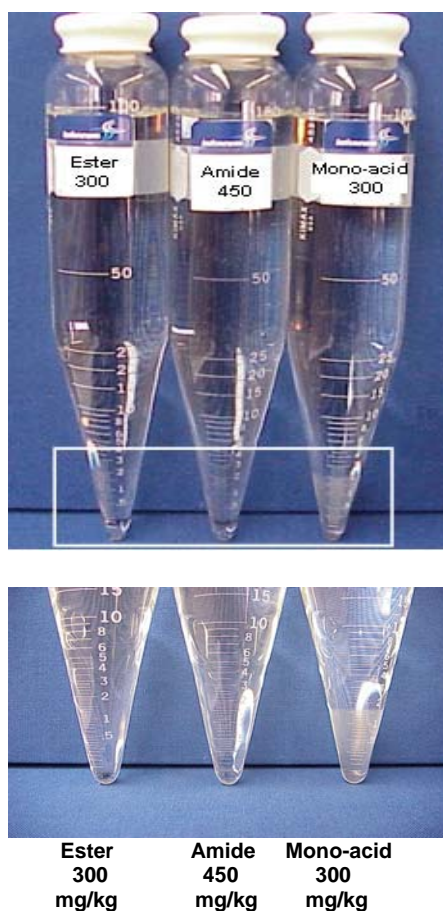


Figure 13: Interaction of sodium naphthenates with fatty acids and other lubricity additives

The same experiment was repeated using a di-acid and the results were in line with those reported for the mono-acid experiment.

5.3.2 TEST 2: INTERACTION OF SODIUM NAPHTHENATES WITH FATTY ACIDS AND OTHER LUBRICITY ADDITIVES AND THEIR FILTER BLOCKAGE POTENTIAL

5.3.2.1 TEST CONDITIONS

The same experiment was repeated and the fuel samples were tested in a filtration rig method used in the petroleum/fuel industry, IP 387 (Navy Rig Test), as a “screening test” to assess potential filter blocking from any interaction. As the fuel samples were 100 mls in volume, the amount of fuel filtered in IP 387 was reduced from the specified 300 mls, but all other test method parameters were unchanged: 20 ml/ minute fuel pumping rate, filter porosity/diameter, etc. The modified procedure, therefore, filtered 100 mls of fuel in 5 minutes, versus 300 mls in 15 minutes. Failure criteria were unchanged: filter $\Delta P > 105$ kPa, or failure to pass/filter the 100 mls of fuel within 5 minutes.

In order to understand how the interaction phenomenon occurs over time, the filtration experiment has been done after one hour of doping the fuel and after five days at 40 °C, the latter uses the same conditions applied to the experiment reported above.

5.3.2.2 RESULTS

The results are presented in figures 14 and 15. The results indicate that the reaction between the mono-acid lubricity additive and the metal naphthenate salt can occur quite readily.

After one hour, the level of insoluble material formed is enough to impair the filtration of the diesel fuel. The sodium salt is clearly more critical. However, the calcium soap also shows filtration problems at the higher additive treating level. At the lower, more commercially realistic additive treat rate, interaction with sodium remains – but is less severe, and is no longer evident for calcium. The data after five days at the higher acidic additive treating level show the same trend, the filtration is reduced for both metals, with sodium being more severe; neutral chemistry additives show no interaction. The same screener filterability assessment was carried out with 50 ppm of di-acid and the result as for the centrifuge experiment above, are consistent with – but more severe than with the mono-acid lubricity additive. Overall these tests indicate acidic additive types can potentially interact with fuels containing sodium or calcium ions, and could explain a possible source of the sodium soaps found present in internal injector deposits.

Lubricity Additive Interaction with Sodium and Calcium

Modified Navy Rig: Delta-P @ 100ml or @ No-Flow
 Tested 1-hour after blending and storage @ 40°C

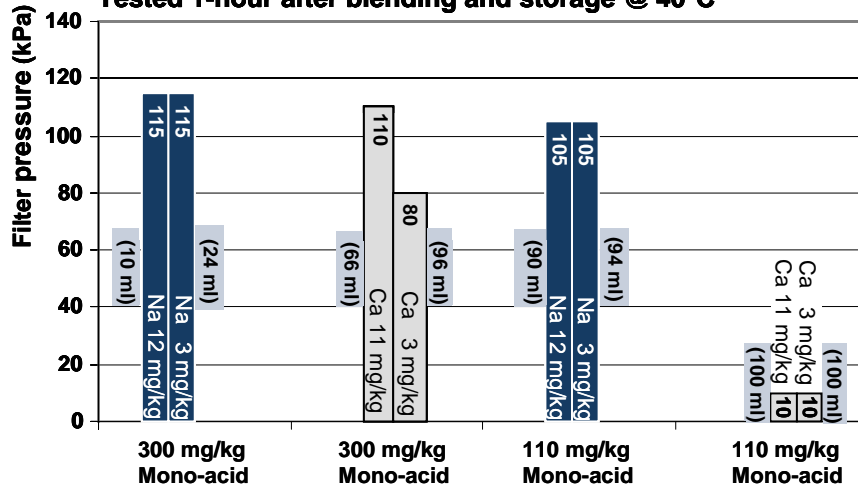


Figure 14: Interaction of sodium and calcium naphthenates with fatty acids at different treat rates and their filter blockage potential, tested 1 hour after blending and storage @ 40 °C (filtration volume in brackets)

Lubricity Additive Interaction with Sodium and Calcium

Modified Navy Rig: Delta-P @ 100ml or @No-Flow
 Tested after 5 days of storage @ 40°C

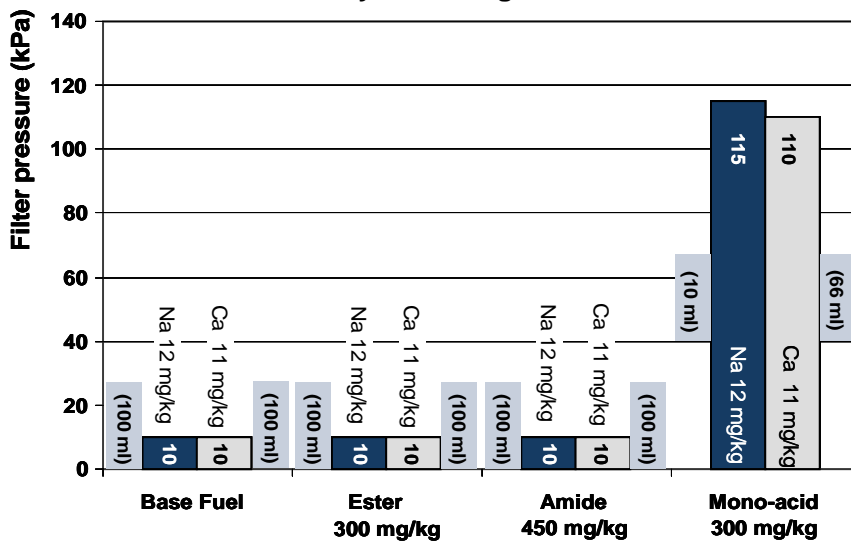


Figure 15: Interaction of sodium and calcium naphthenates with fatty acids and other lubricity additives and their filter blockage potential, tested after 5 days of storage @ 40 °C (filtration volume in brackets)

5.3.3 TEST 3: UPTAKE OF SODIUM BY DIESEL FUEL AND FAME BLENDS AND THE INFLUENCE OF TALL OIL FATTY ACID

5.3.3.1 LABORATORY TEST CONDITIONS

Two different diesel fuels A and B were used. Both were EN 590 standard diesel without FAME. Diesel fuel A (B0) was blended with 5, 10 and 20 % FAME

(EN 14214). Additionally, two B5 fuels (samples C and D) were collected from filling stations also complying with EN 590. Each fuel was vigorously stirred over excess solid sodium chloride or, alternately, treated with a saturated aqueous sodium chloride solution for 12 hours. Afterwards, sodium chloride was allowed to settle for 4 hours. The overlaying phase was decanted in a tube for centrifuging. The sodium content of the fuel was determined by ICP-OES [4].

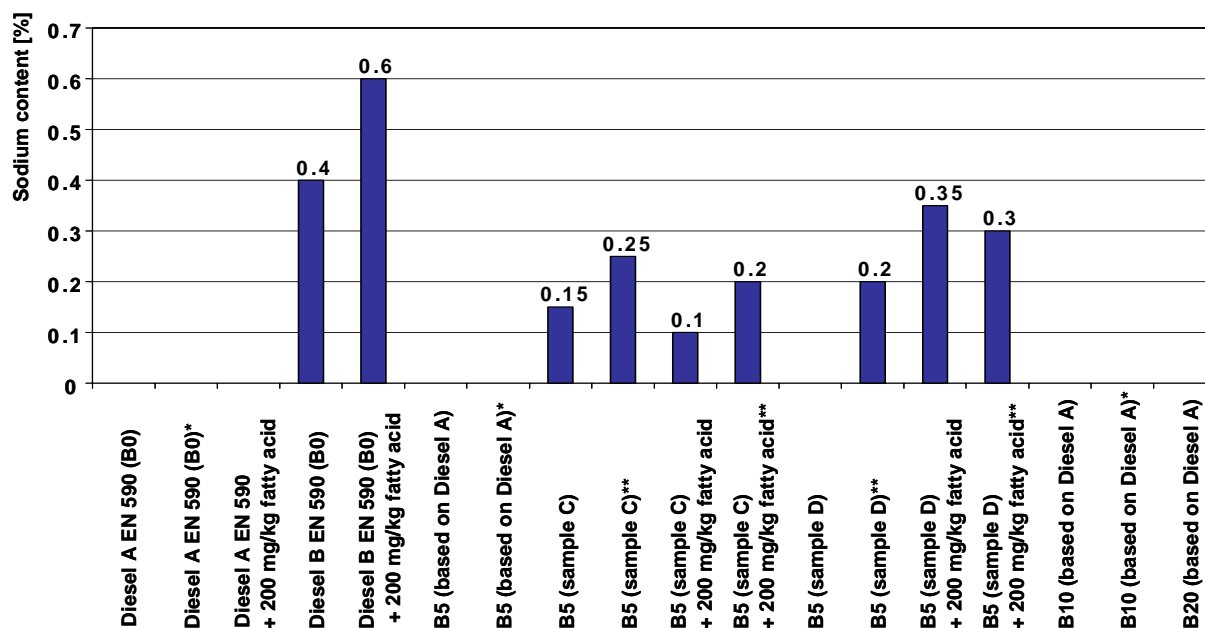


Figure 16: Sodium chloride uptake by fuels after 12 h stirring over a bottom layer of solid sodium chloride or saturated sodium chloride solution at room temperature and at 100 °C. Samples treated with saturated sodium chloride solution are marked with an asterisk, those stirred at 100 °C with two asterisks.

Samples of these fuels were additionally treated with 200 mg/kg of tall oil fatty acid, consisting of a mixture of C18 fatty acids.

5.3.3.2 RESULTS

After stirring for 12 hours at room temperature, no uptake of sodium was observed in diesel fuel A even if FAME was admixed (figure 16). The detection limit for sodium in the fuel was < 0.1 mg/kg. Diesel fuel B had a sodium content of 0.4 mg/kg that could be further increased to 0.6 mg/kg when 200 mg/kg tall oil fatty acid was added prior to sodium chloride treatment. Both B5 blends collected at the filling stations (samples C and D) absorbed traces of sodium at ambient or elevated temperature, respectively.

5.3.4 CONCLUSION FROM THE EXPERIMENTS

The solubilisation of sodium chloride in diesel fuel and FAME blends was demonstrated. Traces of sodium can be dissolved in diesel fuel and in FAME blends. The uptake of sodium depends on the base diesel quality and can be influenced by naphthenic and fatty acids. The deposit forming tendency increases when both, naphthenic and fatty acids are present.

These presented results indicate that sodium can be carried already by FAME-free diesel fuels. FAME blending imposes a further risk of producing sodium impurities by residual catalyst of the esterification process.

The composition of the sodium containing deposits inside high pressure injection systems was confirmed analytically. They consist of either sodium fatty acid soaps or sodium chloride.

Sodium fatty acid soaps are found in the entire fuel system. If fatty acids interfere with traces of dissolved sodium ions, the resulting soaps are less soluble and fall out of diesel fuel.

The transportation of sodium chloride into the injection equipment as well as the way of its deposition, however, still remains unclear. The colourless sodium chloride crystal cubes on the metallic surface on the injector valve needle shown in figure 11 suggest a crystallisation from a co-existent free water phase.

6 GENERAL CONCLUSION

Deposits in the fuel injection system can cause severe operational problems leading to customer complaints. The situation is expected to get more serious in the future since more advanced injection system technologies, developed to help meet future emission standards, impose additional requirements on fuel quality. The further increase in injection pressure leads to more thermal stress on the fuel. The higher temperature accelerates fuel oxidation and also means a higher risk of deposit formation by chemical side reactions of fuel components and additives. Additives will play an increasing role in supporting fuel quality requirements in future e.g. by

improving oxidation stability, ensuring nozzle cleanliness and giving corrosion protection. Therefore, it becomes increasingly important that their application in the field is carefully checked with regards to undesired side effects.

Acidic based additives can be involved in two different deposit forming mechanisms:

- Generating soaps with metal ion impurities, especially sodium
- Chemically reacting with the functional groups of additives, demonstrably with detergents of the PIBSI class.

Attention must also be paid to produce fuels with adequate oxidation stability to avoid deposit formation by

- dissolved ageing polymers that drop out of solution or are subjected to resinification
- chemical reaction of formic acid, one of the most aggressive ageing acids, with certain polar additives.

Fuel cleanliness will also play an important role. Metallic impurities like sodium must be excluded as far as possible. Since concentrations as low as 0.1 mg/kg sodium cannot be analytically controlled on a routine basis, sodium sources

need to be strongly restricted, e.g. during fuel production (FAME) or fuel treatment (drying of diesel fuel). The concentration of contaminants and additives in fuels is certainly very low. However, the potential for deposit forming must not be neglected as the resulting sediments accumulate over time during engine operation, and the total amount of deposit needed for disturbing the highly precise dynamic response of the fuel injectors is also small.

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