

Characterization of Damaging Biodiesel Deposits and Biodiesel Samples by Infrared Spectroscopy (ATR-FTIR) and Mass Spectrometry (TOF-SIMS)

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ABSTRACT

Biodiesel contains a variety of compounds, depending on the production and the provenance of the fuel. During the production process and usage, some of these compounds can form deposits (nozzle tip deposits or internal diesel injector deposits: "IDID"), which may lead to severe problems, such as corrosion, filter blockage and other technical issues. To deal with these difficulties, it is essential to exactly determine the components of these deposits. Most analytical methods used before, require complex preparations and result in limited information of the deposit material. Using infrared microscopy (ATR-FTIR: Attenuated-Total-Reflection Fourier-Transform-Infrared-Spectroscopy) or mass spectrometry (TOF-SIMS: Time-of-Flight Secondary-Ion-Mass-Spectrometry), a direct analysis of the original deposit material is possible.

In order to analyze the chemical composition of the deposits, samples were taken from affected engine parts and filling stations and examined with a TOF-SIMS instrument and a common infrared microscope. Infrared investigations of the engine parts hint to the presence of carboxylic acid salts and mass spectra of the same samples indicate various organic compounds, partly based on polyisobutylene succinimides ("PIBSI"). In the spectra of plugged fuel filters peak-pattern of different sterol glucosides and related compounds are observed. The analyses of directly taken biodiesel samples reveal ingredients such as fatty acid methyl esters (FAME) and sterol esters among other things, so that very detailed descriptions of the fuel constitution are possible. Altogether these investigations show that the combination of infrared spectroscopy and TOF-SIMS is a powerful tool, which provides a large amount of information in order to gain a detailed insight in the formation of these deposits.

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INTRODUCTION

During the production and the use of biodiesel, the formation of deposits is frequently observed. In all parts of diesel engines (gear-wheels, injection valves, spray nozzles, metal rings etc., see [figure 1](#)) these deposits can lead to serious problems, like loss of vehicle drivability up to complete failure of the engine. The exact root cause or formation mechanism of these nozzle tip and internal diesel injector deposits (IDID) are not clarified. More insight in the formation of these deposits, requires as much exact information of their chemical composition as possible. Biodiesel is a natural product, thus various components are present in different amounts depending on the source and the processing of the fuel. Besides the main component - fatty acid methyl esters (FAME) - biofuels may contain a variety of compounds:

- sterol glucosides SG
- acyl glycerols AG
- acylated sterol glucosides ASG
- free fatty acids FA
- various compounds (free sterols, sterol esters SE)
- inorganic and organic sodium compounds



Figure 1. Different components of diesel fuel injection pumps with brown deposits on the surface: injection valve and spray nozzle, different metal rings (inlet piston /port of the fuel feed supply system), internal rotor and small part of a magnetic valve.

It is known that even small amounts of these compounds may cause severe problems, such as bad filterability, filter blockage, corrosion and technical issues, like deterioration of injection precision.

behavior and the spray accuracy. Former investigations - mainly based on infrared spectroscopy - roughly hint to three different kinds of deposits¹:

1. sodium-based salts and soaps
2. insoluble residues and oxidation products of the fuel itself
3. organic polymeric compounds originating from additives (e.g. PIBSI)

In contrast to vibration spectroscopy, direct mass spectrometry of such deposits offers much more and detailed information about the deposit composition. Previous investigations using TOF-SIMS provide relative little information and were limited to inorganic deposit components^{2,3}. Several FTIR investigations are concerned with the PIBSI additive^{1,6} but rarely in direct combination with TOF-SIMS.

As the observed and investigated failures of diesel engines in this article are mostly connected with deposits on the nozzle or in the internal diesel injection system (parts 1 and 2) or in the fuel filters (part 3) the analyses focus on the whole failure chain of the injection system up to the direct comparison with the non-volatile residue of actual biodiesel samples (part 4).

In comparison to former investigations the present article concentrates firstly on the main advantages of TOF-SIMS technology: the detection of nearly all inorganic and organic molecules with very high detection sensitivity and up to high molecular weights. Secondly the two important methods TOF-SIMS and FTIR, that have mostly been used isolatedly for the investigation of biodiesel deposits, have now been used in a complementary study of exactly the same sample materials.

TASK

Since most analytic methods require highly complicated preparations in order to isolate the various individual components of biodiesel and its deposits, the analyses of these deposits are not straightforward. The sticky deposits to be analyzed are mostly insoluble in the typical solvents used in most laboratories, but for nearly all conventional analyzing methods (e.g. Gel-Permeation-Chromatography GPC or Gas-Chromatography-Mass-Spectrometry GCMS) the contained chemical compounds must be soluble in the extraction solvent, where, ideally, they should have a certain concentration and disturbing matrix compounds should be removed. Furthermore, many deposits have been analyzed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The SEM-investigations are very useful, because SEM-images give a valuable impression of the deposit morphology so that information about the deposit structure and origin can be obtained. Nevertheless the chemical information got by EDS is limited to elemental analysis and a detection probability above 0.1 atomic %.

Contrarily by means of infrared spectroscopy or mass spectrometry it is possible to analyze the deposits directly without the difficult intermediate steps like solvation or extraction. Also detached deposits can be investigated by simply placing them on cellulose or metal substrates as target holder.

By using TOF-SIMS measurements, it is possible to analyze deposits on parts of the engine, biodiesel deposits as well as actual biodiesel samples directly with a one-step-preparation. ATR-FTIR spectra reveal further information concerning main components and the ratio of organic/inorganic compounds.

EXPERIMENTAL SECTION

Samples

Parts of engines and biodiesel samples were received from field failures in western Europe. In most cases residues / deposits on injector needles and other motor components were directly analyzed after cleaning the parts with heptane or hexane. Additional commercial biodiesel samples were collected from different filling stations in northern Germany (brand filling station and free filling station, obtained directly from fuel dispenser). In this case the preparation method uses cellulose substrates or the fuel itself deposited on a metal target.

Methods

Mass spectra of the different samples were obtained with a TOF-SIMS V instrument⁴ (figure 2). The samples were irradiated with Bi⁺ primary ions in form of a pulsed ion beam (→ Pulsing Unit for the primary ions) under an incident angle to the sample surface of 45°. The energy of the primary ions was 25 keV with a typical beam current of 1.5 pA. The analyzed area was in the range of 100 x 100 µm to 500 x 500 µm corresponding to the geometry of the sample. As most of the samples are insulators, charge compensation with low energy electrons (25 eV, electron flood gun) have been carried out. Due to focusing optics and raster unit the lateral resolution of the primary ion beam was below 1 µm. During the ion bombardment elements, molecules and molecular fragments are ionized and desorbed from the surface and directly extracted by high voltage (2 kV) into the analyzer⁵. Here the particles now designated as secondary ions transmit an ion-mirror (reflectron), where the different initial start energies of the ions are compensated. The ions are counted time-resolved at the detector i.e. signal intensity versus time-of-flight that is converted into a mass spectrum. Mass resolution (m/dm) up to 15000 is achieved, so that a clear identification of elements and molecules is possible.

ATR-FTIR spectra were measured on a common infrared microscope (Tensor 27 with Hyperion 2000 IR microscope from Bruker Optik GmbH, Ettlingen). The lateral resolution of the instrument is about 10 µm under ideal conditions (about 20 - 50 µm for typical industrial samples). Samples have been investigated in the ATR or in the transmission / reflection mode.

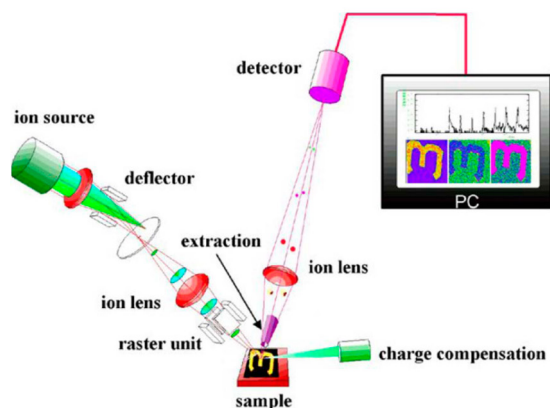


Figure 2. Scheme of a TOF-SIMS instrument and a picture of the used TOF-SIMS V apparatus.

RESULTS AND DISCUSSION

1. Deposits on Injection Valve Needles

After operation and thermal stress of the fuel injection system, deposits are often observed on the surface of injection valve needles (see [fig. 3](#) and [4](#)).

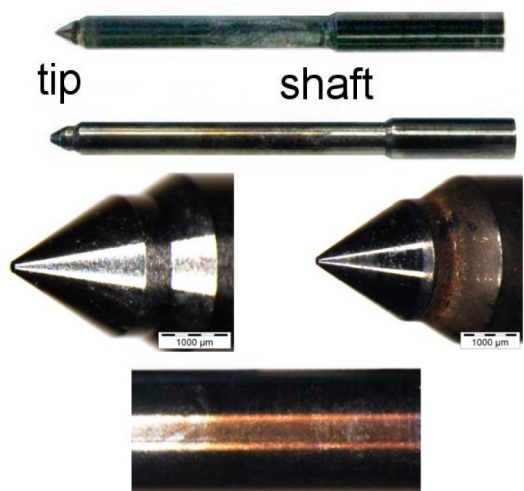


Figure 3. Pictures of different valve needles with lateral inhomogeneous deposits on shaft and tip (upper rows). Whereas on the tip of the needle a relative thick coverage is detected, there are circular discolorations on the shaft (bottom row).

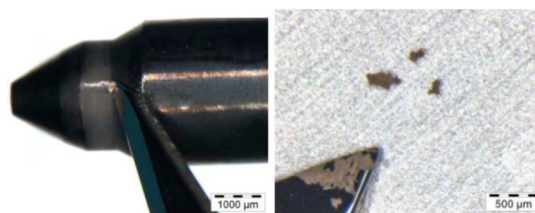


Fig. 4. Sometimes the coverage on the tip is thick enough to prepare it on another target.

Micro FTIR-ATR investigations of the mostly brownish and redish colored deposits in different positions of the valve needles often result in poor or non- resolved spectra (see [fig. 5](#), above) that are not really diagnostic. This is partly due to the fact that the coverage on the metal substrate of the needle valve is too thin for infrared spectroscopy and may hint in some other cases to carbonaceous material. Only vibration bands at $3000\text{--}2800\text{ cm}^{-1}$ and at 1560 cm^{-1} can be resolved but the band intensities are very small so that they can only give hints to aliphatic CH species (compounds with long alkyl chains) and carboxylic acid salt.

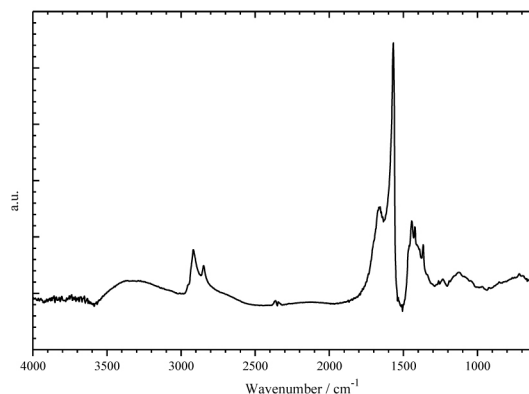
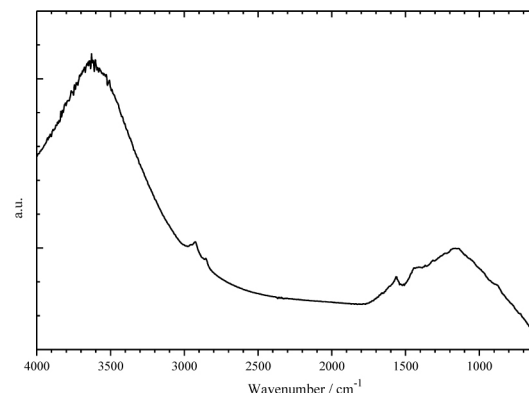


Figure 5. ATR-FTIR spectra of an injection valve needle in areas with thin (above) and thick (below) deposits.

Otherwise in a needle area with thick deposits, the infrared spectra show an absorption band at 3300 cm^{-1} (OH functionality) and specific bands especially at 1556 and 1449 cm^{-1} that can be clearly deduced from the presence of carboxylic acid salt (different metal soaps are possible, see [fig. 5](#), below).

Mass spectrometry of these residues shows predominantly inorganic compounds such as sodium-hydroxides, -cyanides, -cyanates, -carbonates and -sulfates (mostly at the needle tip, [figure 6](#)).