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On the mechanism of deposit formation during thermal oxidation of mineral diesel and diesel/biodiesel blends under accelerated conditions

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HIGHLIGHTS

- Investigation of mechanism of the formation process of solid (bio)diesel deposits.
- Fuel degradation products start cross-linking processes upon heating above 150 °C.
- Molecular weight of solid deposits depends on temperature and reaction time.
- Critical temperature for insoluble deposits is lower for B20 compared to B0.
- Solubility of B20 deposits in THF depends on reaction temperature and time.

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ABSTRACT

The influence of temperature and time on the formation process of solid deposits after accelerated degradation of mineral diesel (B0) and a biodiesel blend (diesel/rapeseed methyl ester blend (B20)) is studied in model experiments. We show that the formation of deposits strongly depends on the temperature to which the fuel is exposed. Heat-treatment of the fuel samples at above 140 °C for longer than 6 h under constant air flow leads to the formation of colored, homogeneous solutions containing polar, high molecular weight oxygenated fuel products (mOFP). The formed mOFP are precipitated in *n*-heptane and subsequently analyzed. Correlations between temperature and duration of the heat-treatment and the amount of precipitated mOFP as well as the acidity of the fuels and spectroscopic data of the fuels are elucidated. Upon heating of isolated mOFP precursors at temperatures above 150 °C solid fuel deposits are formed. Analysis by size exclusion chromatography shows that, depending on temperature and reaction time, the molecular weight increases, the molecule become branched and ultimately cross-linked compounds are formed. At temperatures of up to 200 °C the B20 deposits remain completely soluble in a common solvent with an intermediate polarity such as tetrahydrofuran (THF), independent of reaction time. With increasing temperature and duration of the heat exposure the solubility becomes more and more reduced until eventually complete insolubility is reached. A comparison between heat treated model compounds and deposits isolated after completion of engine testing experiments is made. The implications of the improved understanding of the deposit formation process onto new design rules for possible next-generation injector designs are discussed.

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1. Introduction

Fuel circulating in fuel systems of modern diesel engines is compressed to high pressures and undergoes thermal stress up to 200 °C [1]. At such elevated temperature the presence of oxygen

leads to thermal-oxidative degradation processes and property changes of the fuel. Particular unburnt fuel molecules can recirculate several times within the fuel system until they are injected into the combustion chamber. This leads to a stepwise thermal-oxidative degradation of these molecules. Moreover, fuel can degrade during storage or in the tank system. Products formed in such degradation processes can cause corrosion, filter clogging and deposit formation on injector parts, which in turn will have

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a negative impact onto the engine performance and might lead eventually to complete failure of the fuel injection equipment (FIE) [2,3]. The high injection pressures and increasing fuel temperatures, which are typical for modern diesel engines, exacerbate the problem. Over the past years, the increased use of blends between mineral diesel and biodiesel has led to raising concerns about the formation of deposits, as biodiesel has a much lower thermal stability as its conventional counterpart [4]. Particularly, the formation of deposits on injector parts, especially the nozzle spray holes, could have detrimental impacts on the engine performance. As the injection holes have only very small dimensions (i.e. typical diameters are currently only around 100 μm with a current trend for a decrease to 80 μm) even thin film deposits with thicknesses in the micron range can destroy the injection pattern seriously. Thus, the combustion process within the combustion chamber is disturbed, which results in a deterioration of the engine performance, higher fuel consumption and amplified emissions [5,6]. Mineral diesel consists mainly of hydrocarbon compounds, whereas biodiesel is essentially made up of long-chain mono- or polyunsaturated fatty acid methyl esters (FAME) [7]. As in both fuels long-chain aliphatic chains are key components, similarities of the behavior exist. There are, however, also some important differences. Due to the high amount of unsaturated groups in the FAMEs and presence of the carbonyl groups, biodiesel shows a higher susceptibility to oxidation and degradation than mineral diesel fuel [8]. Mineral diesel and biodiesel fuels both undergo an autoxidation process at temperatures lower than 260 $^{\circ}\text{C}$ [9–11]. The autoxidation follows a radical chain reaction mechanism [12] where initiator radicals are firstly generated during chain fracture (I^{\cdot}) leading e.g. to formation of allylic or bis-allylic fatty acid radicals (F_A^{\cdot}). Oxygen can react at these sites to form peroxide radicals ($-F_A\text{OO}^{\cdot}$) [13], which can undergo further thermally induced reactions. Through such processes allylic hydroperoxides ($-F_A\text{OOH}-$) [14], cyclic peroxides [15] and fatty acid radicals ($-F_A^{\cdot}$) are generated. Follow-up reactions of hydroperoxides can form polar secondary oxidation products like alcohols, ketones, aldehydes, and short chain carboxylic acids [15]. In one reaction pathway, at temperatures between 250 $^{\circ}\text{C}$ and 300 $^{\circ}\text{C}$ or more, polyunsaturated fatty acid degradation is followed by (4+2)-cycloaddition (Diels–Alder reaction) resulting in the formation of oligomeric compounds and eventually macromolecules [9,10]. Furthermore, aldehydes and ketones can react via aldol-condensation to connect different molecules so that also strongly branched macromolecules are formed [15]. The autoxidation process of hydrocarbons (mineral diesel) leads also to the formation of hydroperoxides as primary oxidation products [11] and through further bond formation subsequently to macromolecular products. It is important to consider that macromolecular products can be formed from both fuels (mineral diesel and biodiesel). These formed polar macromolecules are easily soluble in more polar solvent such as THF, but can be precipitated from non-polar compounds such as n-heptane. The formation of mOFP is much stronger if mineral diesel is blended with biodiesel [1,15]. Numerous studies about the oxidative stability of mineral diesel and pure biodiesel are reported in the literature [9–11,14–18]. A challenging problem caused by degraded fuel is the decreased lifetime performance of diesel injectors due to deposit formation. Deposit formation is thus discussed intensively in the context of injector technology [3,5,19–23]. Five different deposit formation mechanisms have been discussed [21]. These are the formation of (i) carboxylates [3,22,24], (ii) organic polymeric amides [3], (iii) pyrolysed carbon [25], and (iv) macromolecular oxygenated fuel products [1]. Furthermore, mOFP, soot and reactive combustion gases can form coked deposits (v) inside and outside of the nozzles [5,26]. mOFP have been identified as an important species regarding deposit formation. Nevertheless, the entire formation process from fuel to mOFP based

deposits is still not well understood. This paper reports on a model study for the formation of deposits during thermal degradation of mineral diesel and blends of this diesel and biodiesel under accelerated laboratory conditions. To help understanding the details of the mechanism, fuels were used in this study which did not contain any additives, which are usually added to commercial fuel products. One of the goals of the addition of such compounds is to reduce the extent of degradation during the thermal–oxidative processes. The correlation between the temperatures of fuel treatment and the mass of mOFP, the total acid number, and spectroscopic data under airflow is studied. Additionally, it is investigated what happens if the fuel containing the mOFP dries while it is continuously heated. The implications of the deposit formation process onto the fuel injection behavior are discussed.

2. Materials and methods

2.1. Materials

Mineral diesel produced by Shell (DIN EN 590) without FAME content and without additional additives was utilized. Biodiesel (Rapeseed methyl ester [RME]) was supplied by ADM Hamburg, according to DIN EN 14214. RME is used in our studies since RME is currently the most widespread type of biodiesel in Europe. Acetone, methanol (both $\geq 99.8\%$), n-heptane ($\geq 99\%$), tetrahydrofuran (THF) (HPLC grade) and toluene ($\geq 99.9\%$) were purchased from Merck and used without further purification.

2.2. Methods

2.2.1. Test procedure

A round-bottom flask was filled with 200 mL of fuel and placed in a heated silicone oil bath. The required temperature of the oil bath was monitored online by a temperature control unit. Gas bubbling through the fuel was performed with a rate of 20 L/h using a Pasteur pipette made from glass. For experiments performed under inert conditions nitrogen gas was used to fill the resuming atmosphere inside the beaker. The volatile components were not collected. After each experiment 40 mL aliquots of fuel was withdrawn, cooled to room temperature, and used for mOFP precipitation. To this, the aliquot was diluted with 160 mL n-heptane. After keeping the solution for 24 h at room temperature, the supernatant liquid was subtracted and the precipitated mOFP were dried for 1 h at 110 $^{\circ}\text{C}$ and weighed. The mOFP were then dissolved in a mixture of methanol/acetone/toluene (approx. 1:1:1, v/v/v) for easier handling. 40 μL of this mOFP solution were dropped onto a polished (final stage: 1 μm diamond suspension) 18CrNi8 sample. Subsequent heat-treatment under air atmosphere was performed in a drying oven (Heraeus Vötsch Industrietechnik). Afterwards, each sample was dipped in THF for 15 min performing solubility experiments. The residual insoluble deposits were separated by disposable PTFE syringe filters (preparation: washing with THF, drying at 90 $^{\circ}\text{C}$ for 3 h). Prior to weighing all filters were dried again for 3 h at 90 $^{\circ}\text{C}$.

2.2.2. Characterization

The FT-IR spectra were recorded with a BioRad Excalibur FTS 3000 spectrometer by Varian. Measurements were done for wavenumbers between 450 cm^{-1} and 4000 cm^{-1} at a resolution of 2 cm^{-1} . The FT-IR spectra in Fig. 10 were recorded with a Equinox-55-1 spectrometer by Bruker at Robert Bosch GmbH. Wavenumber range was measured between 600 cm^{-1} and 4000 cm^{-1} at a resolution of 2 cm^{-1} . UV–vis spectra were measured with a Cary Bio 50 spectrometer produced by Varian. All data were collected in the 190–500 nm range. The samples were dissolved in

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