



Polar nitrogen-containing aromatic compounds as carriers of natural diesel lubricity



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HIGHLIGHTS

- Ionic liquid extraction was able to extract polar compounds from a gasoil.
- This verified the hypothesis of diesel lubricity.
- It was possible to refute the hypothesis that sulfur compounds in diesel affect its lubricity.
- Additivation of selected polar compounds was able to restore lubricity of diesel fuel in some cases.
- Nitrogen-containing aromatic compounds were identified to have a strong effect on lubricity.

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ABSTRACT

Hydrodesulfurization (HDS) reduces the original lubricity of diesel fuel on which fuel injection equipments (FIE) rely for proper operation and lifetime. In technical terms this problem was solved by addition of lubricity additives to low and ultra-low sulfur diesel. In scientific terms there is no clear final conclusion on the role of neither sulfur- nor polar oxygen- and nitrogen-containing compounds. In this study, polar compounds were extracted from a gas oil by an ionic liquid so that the fuel was not saturated by hydrogen like in the industrial HDS process. Stepwise extraction and measurement of sulfur and nitrogen contents as well as lubricity revealed a significant correlation between lubricity and nitrogen content. For investigation on the molecular structure of the lubricating nitrogen compound, selected model compounds with different structural features were added to an ultra-low sulfur diesel (ULSD). The results indicate that the combination of a diaromatic base structure with a polar substituent and a nitrogen heteroatom exhibits excellent lubricity improvement superior to those structures lacking one or more of these three properties. A three-stage tribological model for the boundary lubrication by such compounds is proposed in this paper. These compounds are identified as the main carrier of original diesel lubricity which are removed by the industrial HDS process.

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1. Introduction

Diesel combustion engines require fuel injection equipment which injects precise amounts of diesel fuel in defined spray patterns into the combustion chamber [1]. The highly-loaded mechanical sliding and rolling components of these high-pressure pumps and injector nozzles require diesel fuel with adequate lubricity in order to maintain functionality and endurance requirements [2].

Modifications of fuel chemistry by first attempts to deep-desulfurization reaching sulfur contents of 10 ppm, like the introduction of the famous Swedish Class I diesel in 1991, resulted in

unexpected sudden failures of diesel pumps by severe adhesive wear [3–5]. This new severe desulfurization process in the Gothenburg refinery by a two-stage hydrogen-treatment altered the lubricating property of the diesel fuel in a way to which fuel pumps were not prepared for. In this context the term of fuel lubricity was defined as “the ability of a fuel to prevent or minimize wear in diesel fuel injection equipment” [6]. This new lack of lubricity was overcome by the addition of lubrication-enhancing substances to the fuel, so-called lubricity additives by petroleum companies and their additive manufacturers [7,8].

Parallel to efforts to restore diesel lubricity by adequate additive technology, investigations were carried out in order to find the root cause of lubricity decrease by hydrodesulfurization (HDS). Since most sulfur compounds are removed by HDS and desulfurized fuels

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posses weak lubricity, the postulation of sulfur as carrier of diesel lubricity was obvious. In the field of lubricant oils and greases for bearings, gears and engines, specific sulfur-containing compounds are widely-applied [9]. These so-called extreme-pressure and anti-wear additives prevent severe wear and failure of sliding components by forming protective reaction layers. Lately there has been a direct comparison of gas oil (main blending component of diesel fuel) samples right before and after the HDS reactor [10]. The lubricity of three different gas oil samples was measured by the HFRR method [11] and in terms of the incipient scuffing load (ISL) in the High-Temperature Oscillating Machine (HiTOM) with a reversing cylinder-on-plate sliding contact. During the HDS process of these gas oils their sulfur content was reduced from 1203–3645 ppm down to 8–12 ppm and their nitrogen content from 15–164 ppm down to 8–35 ppm. Before the HDS the HFRR lubricity values WS1.4 reached around 400–500 μm , whereas after HDS only poor lubricity values around 550–650 μm were found. The HiTOM load-carry capacity ISL was only tested for one sample oil and decreased from 3250 N to 1750 N. Hence, the clear proof was given that the HDS process is responsible for the decrease of lubricity. The role of sulfur was investigated by several studies which added different sulfur compounds to diesel samples and compared the lubricating property [12,13]. Mercaptans and sulfides (dibenzyl disulfide, cyclopentyl sulfide and benzyl mercaptan) increased wear in the HFRR at concentrations of 100–1000 ppm. Di-tertiary butyl disulfide and benzothiophene at sulfur levels of 360 ppm increased wear in pump bench test and with the BOCLE tribometer [14]. In terms of HFRR lubricity benzothiophene, dibenzothiophene and 4,6-dimethyldibenzo-thiophene showed no significant ability to restore the lubricity of deep-desulfurized gas oil at sulfur contents of 1000 ppm [10]. Nevertheless, dibenzothiophene (1000 ppm S) exhibited the potential to double the load-carrying capacity in the HiTOM [10]. Certain sulfides also increased the scuffing load of jet fuel in the SLBOCLE tribometer [15]. Hence, there is no general judgement whether sulfur compounds in their huge variety have a negative, positive or no effect in the different tribological test methods for diesel fuel. Since there is no clear proof that sulfur compounds in diesel fuels are the main carrier of lubricity, other compounds which are also removed by HDS must be responsible for natural diesel lubricity.

During the hydrogen treatment in the desulfurization reactor, organic nitrogen compounds are also removed [16]. The comparison of gas oil samples before and after hydrotreatment showed a correlation of lubricity with the nitrogen content [10]. Indole, pyrrole, quinoline and pyridine significantly improved the lubricity of hydrotreated diesel at extremely high nitrogen contents of 10,000 ppm [12]. Nitrogen-containing aromatic compounds exhibited an even stronger lubricity-enhancing ability when the molecules also contained oxygen atoms [17]. 8-Hydroxyquinoline and 1,4-hydroquinone as carriers of nitrogen and oxygen were shown to be able to improve lubricity [12].

In this paper, experiments were carried out in which sulfur and nitrogen compounds were removed from a gas oil sample with an ionic liquid extraction technique. During the extraction cycles HFRR lubricity was measured and correlated with the remaining nitrogen and sulfur contents. Furthermore, typical model compounds as representatives for nitrogen- and oxygen-containing aromatic compounds were added in realistic levels to an ultra-low sulfur diesel fuel to evaluate their contribution to lubricity.

This paper aims to increase the understanding about the origin of diesel lubricity with special emphasis on the contribution of polar nitrogen- and oxygen-containing aromatic compounds. Furthermore, the role of sulfur compounds as lubricity carriers shall be questioned. These findings shall contribute to scientific understanding and shall also provide knowledge for practical refinery processes.

2. Material and methods

2.1. Lubricity evaluation with high-frequency reciprocating rig (HFRR)

In this study the HFRR standard test method according to ISO 12156-1 [11] for assessment of diesel fuel lubricity was used (see Fig. 1). All measurements were carried out at least twice and corrected wear scar diameter values WS1.4 are displayed here.

2.2. Removal of sulfur and nitrogen compounds by ionic liquid extraction

Ionic liquids (IL) are substances which consist of ions only, like salts, but which are in the liquid state below 100 °C. Because of their high polarity specific ionic liquids can be used for the extraction of sulfur from petroleum fractions [19,20] (see Fig. 2).

Studies have already been carried out applying column chromatography with polar silica columns to generate diesel fractions of varying polarity [12,21]. In this experiment sulfur and nitrogen compounds were extracted by the ionic liquid AMMOENG 102™ from the former company Solvent Innovation (now part of Merck). This specific ionic liquid was selected because good results could be achieved of its ability to extract sulfur compounds from gas oil [20] and because of its availability. AMMOENG 102™ consists of the anion ethyl sulfate and an ammonium cation which is substituted by one hydrocarbon chain from tallow and by two polyethylene glycol chains (Fig. 2). This prehydrotreated gas oil had an initial sulfur content of 110 ppm and an initial nitrogen content of 80 ppm (Table 3). According to the manufacturer this IL is produced with a surplus of the amine so that the toxic ethyl sulfate is completely used up. To avoid contamination of the gas oil with remaining amine, the IL has to be purified before the sulfur extraction. The purification was carried out by mixing the IL with cyclohexane in a volume ratio of $V_{\text{IL}}:V_{\text{hexane}} = 1:3$ for one hour. The nitrogen content in the used cyclohexane was an indicator for the extracted amine impurities and was measured afterwards. After ten washing cycles the nitrogen content in cyclohexane had decreased from initially 100 ppm down to 7 ppm. Hence, the IL was considered as purified from amine impurities and could be used for the main extraction of the gas oil. In order to achieve a content of remaining sulfur in the gas oil of less than 10 ppm five extraction cycles were necessary. Each extraction step was carried out by mixing the gas oil with the ionic liquid turbulently with a shaft stirrer in a mass ratio of $m_{\text{gas oil}}:m_{\text{IL}} = 1:2$ for 20 min. Polar molecules fractions enrich in the polar IL phase and hence are being extracted from the gas oil. After the mixing procedure the immiscible phases IL and gas oil were separated with a centrifuge. The IL was then discarded and the gas oil sample was analyzed for sulfur and nitrogen content and also for lubricity. The rest of the gas oil which was not used for the latter analyses was then extracted in a further step with fresh IL.

2.3. Determination of nitrogen and sulfur content

Sulfur and nitrogen contents were measured after each step of ionic liquid extraction with the elemental analyzer NS 9000 from ANTEK. Values given here are results of triple measurements.

With this instrument, an auto sampler injects a fuel sample volume of 15 μL into the combustion chamber where the sample is completely combusted in an oxygen atmosphere. Sulfur from the sample is completely oxidized to sulfur dioxide and excited with UV radiation. Water is removed from the gas stream with a membrane dryer. A photomultiplier amplifies and detects the luminescence of excited sulfur dioxide molecules. The absolute sulfur content is determined by calibration with standards of known

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