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Impact of oxygen and nitrogen compounds on the lubrication properties of low sulfur diesel fuels

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Abstract

This paper presents the impact of oxygen and nitrogen compounds on the lubrication properties of low sulfur diesel fuels. It discusses the most recent results, concerning the influence of adding low amounts of 4 specific types of biodiesel, 5 aliphatic amines, 2 tertiarty amides, 10 mono-carboxylic acid esters, 3 acetoacetates and 7 esters of di-carboxylic acids on the tribological behaviour of the steel-on-steel systems, lubricated with low sulfur automotive diesel fuel. Experiments were carried out on the HFRR (high frequency reciprocating rig). The obtained wear results showed that all the various classes of additives improved fuel lubricity.

Keywords: Lubricity; Diesel; Biodiesel; Aliphatic amines; Tertiary amides; Acetoacetates; Mono- and di-cabroxylic acid esters

1. Introduction

Interest in diesel fuel lubricity has escalated since the early 1990s. It was at this time that ultra low sulfur (<20 ppm) Swedish Class 1 and 2 fuels were commercialized and coincident with this, there was an increased incidence of drivability problems (cold starting problems) and fuel injection pump failures. In some cases, these failures took place in passenger cars after only 3000–10,000 km [1]. In Europe and the USA, it was shown that highly refined fuels could reduce the life of distributor type fuel pumps. The field trials and pump rig durability testing of both Swedish Class 1 and 2 diesel fuels showed that their inherent lubricity was unacceptable [2]. Since then, considerable efforts have expended on investigating the lubricity of low sulfur diesel fuels [3–9].

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Diesel fuel injection pumps are lubricated primarily by the fuel itself. Traditionally fuel viscosity was used as an indicator of a fuel's ability to provide wear protection, but since the introduction of low sulfur diesel fuels, even some fuels of higher viscosity have been found capable of producing wear [10]. Past studies showed that diesel fuel lubricity is largely provided by trace levels of naturally occurring polar compounds which form a protective layer on the metal surface. Typical sulfur compounds do not confer this wear protection themselves, rather it is the heterocyclic aromatics and nitrogen and oxygen compounds that are the most important [11–13]. A complex mixture of polar compounds is found in diesel fuel and some are more active than others. The process of hydrotreating to reduce sulfur levels also destroys some of these natural lubricants. Other refinery processes also influence the concentration of the lubricity agents in the final fuel blend [14]. Lubricity additives have been developed to compensate for the deterioration in natural lubricity observed in low sulfur diesel fuels. A moderate dosage of chemically suitable additive is beneficial in most cases, but if the dosage is too high, some common diesel fuel additives can cause fuel injector deposits, water separation problems, or premature filter plugging. These problems are not always identified in the standard fuel specification tests, and result in field problems [15–18].

The first stage of this study includes the evaluation of the lubricating properties of low sulfur diesel fuels containing biodiesel produced from sunflower oil, olive oil, corn oil and used fried oil. Data were generated to identify the minimum concentration of the above specific types of biodiesel, which would provide lubricity improvement down to the 460 μm wear scar diameter (WSD) level [19]. Methylesters of vegetable oils are the most thoroughly studied for boundary lubrication. Past studies indicated that biodiesel produced from rape seed oil and conola oil could serve as an alternative to synthetic additives to meet the lubricity requirements of equipment [20,21]. However, the impact of adding biodiesels prepared from other starting materials, such as sunflower oil, olive oil, corn oil and used fried oil on fuel lubricity has not been examined extensively, although these types of vegetable oils comprise interesting candidates for biodiesel production especially in Southern Europe, where rape seed is not widely cultivated [22].

Biodiesel is easily prepared from vegetable oil triglycerides through the transesterification reaction with methanol [23]. Fatty acids comprise 94–96% of the whole mass of the triglyceride molecule and the beneficial ability of biodiesel on lubrication characteristics of low sulfur diesel fuels could be attributed to the existence of these acids. According to Bowden and Tabor, the addition of a small amount of fatty acid to a non-polar mineral oil or to a pure hydrocarbon can bring about a considerable reduction in the friction and wear. Wei and Spikes [25] observed that a significant wear reduction was produced by fatty acids, introduced into hydrotreated fuel at low concentration: caproic acid (100 ppm) and palmitic acid (300 ppm) [24]. A more recent paper discusses the effect of fatty acids (C_6–C_{18}) at low concentrations (50–750 ppm) in *n*-hexadecane on wear of steel under boundary lubrication conditions [26].

Because of its oxygen content, biodiesel as a fuel generally results in improved combustion quality; it leads to lower HC, CO and particulate emissions while a slight increase of NO_X and aldehyde emissions is observed in some cases. Unfortunately, common biodiesel has a cetane number similar to conventional diesel fuel, which means it offers no improvement to the ignition quality. This is particularly important in the light of the increasing cetane number value in diesel fuel specifications, which the European Union set at 51 (from 49) in January 2000, and is expected to increase.