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Review article

Tribological behavior of diesel fuels and the effect of anti-wear additives

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HIGHLIGHTS

- ▶ Main reason for the lubricity of diesel fuels is oxygen- and nitrogen-containing polar compounds.
- ▶ Anti-wear additive becomes the prime requirement to be mixed with desulfurized diesel fuel.
- ▶ Biodiesel and chemical polar compounds are the major class of lubricity additives.
- ▶ Anti-wear property of additives increases with increase in unsaturation and hydroxyl groups.

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ABSTRACT

Petrodiesel fuels are complex mixtures whose composition differ from refinery to refinery and according to the type of crude oil processed. They are prepared by blending two types of streams viz. straight run distillate and distillates from upgrading of residues. In order to make diesel fuels to work over a wide variety of working conditions, its properties are fixed to a standard value, which may differ in different countries according to their climate conditions. Also, to reduce pollution, some rules and regulations have been framed so as to limit the amount of harmful components as sulfur, nitrogen in the fuel.

Till 1990s, sulfur was accepted up to a maximum value of 500 ppm. But keeping the green environment in view, the regulations have been made more stringent and presently sulfur should not be present beyond 50 ppm or even less in some countries. So, it is required to be removed through different processes. But during those processes many components responsible for lubricity also get removed, leading to the breakdown of fuel distribution pump, engine failure, etc. So, the lubricity is required to be regained with the help of anti-wear additives. The paper reflects light on different types of bio as well as chemical anti-wear additives as lubricity enhancement in ULSD fuels, is still a challenging task for researchers.

Contents

Abbreviations: ASTM, American Society of Testing and Materials; EPA, Environmental Protection Agency; ULSD, Ultra Low Sulfur Diesel; HiTOM, High Temperature Oscillating Machine; BOCLE, Ball On Cylinder Lubricity Evaluator; HFRR, High Frequency Reciprocating Rig; S BOCLE, Scuffing Ball On Cylinder Lubricity Evaluator; FAME, Fatty Acid Methyl Ester; SBME, Soyabean Methyl Ester; POME, Palm Oil Methyl Ester; EMA, Engine Manufacturers Association; WSD, Wear Scar Diameter.

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1. Introduction

Automotive diesel fuels are complex mixtures whose composition depends on the sources of the crude petroleum, methods of separation and the purification techniques. Essentially they are the mixtures of saturated, olefinic and aromatics hydrocarbons with molecules of carbon C_9—C_{20} in the boiling range of 170–350 °C with minor proportions of sulfur, nitrogen and oxygen containing organic compounds. Diesel fuel is common in two grades: 1-D grade (diesel No. 1), generally a straight run distillate with boiling range 170–270 °C, and 2-D grade (diesel No. 2), the blend of two or more refinery streams including cracked gas oil, heavy naphtha, light and heavy gas oils, etc., with boiling range 180–350 °C. In general, diesel word is used primarily with reference to 2-D grade, since this is the grade, generally used in all on-road vehicles as well as in majority of the off-road applications.

Diesel fuel must satisfy a wide range of engine types, different operating conditions and duty cycles as well as variations in fuel system technology, engine temperatures and fuel system pressures. By controlling specifications and properties, it is possible to satisfy the requirements of millions of compression ignition engines with a single grade of diesel fuel. So, some guidelines have been established internationally for diesel fuel quality by American Society of Testing and Materials (ASTMs), while some countries have their own standards, which may vary slightly from ASTM property limits. ASTM standards are continuously reviewed and updated from time to time.

Diesel fuel is one of the prime focus areas of research for the scientists in order to improve the properties of fuel as per the standard specifications. In the present scenario, the scientists and environmentalists are concerned with ecofriendly fuels worldwide since industrial development brought with its prosperity environmental pollution. Transportation vehicles with hydrocarbon fuel contribute significantly to air pollution through the emission of SOx and NOx from IC engines, which are well known health hazards. The best way to control SOx and NOx emissions is to produce ultra clean fuels in the refinery. So, diesel fuel cannot be used as such, but has to undergo one or more treatment processes such as solvent extraction, caustic treatment and hydrotreating to reduce their adverse effects on environment. Hydrogenation is especially effective in removing sulfur compounds, but during the process polyaromatics, nitrogen- and oxygen- containing compounds and unsaturated components are also removed, which might be responsible for decrease in the lubricity of the fuel [1].

2. Lubricity

Diesel fuels must possess a modicum of lubricating ability to protect pumps and related fuel supply equipment from wear and other tribological problems. Lubricity is of important consideration for most types of diesel fuel injection equipment because these types of pumps rely totally on the fuel for lubrication of their moving parts. The fuel protects the metal parts from wear due to the formation of hydrodynamic film between the rubbing solid surfaces and/or by boundary lubrication. Many researchers believe that the thickness of hydrodynamic film increases with the dynamic viscosity of the fluid, while others are discontented [2,3]. Lucas, the leading fuel injection equipment manufacturer in England explains: "The lubrication of the fuel is not directly provided by the viscosity of the fuel, but by other components in the fuel which prevent wear on contacting metal surfaces". It is also supported by the fact that some low sulfur diesel fuels with higher viscosity have been found incapable of preventing wear [4]. The another type of lubricity i.e. boundary lubricity results by the solid–solid interactions between the impurities present in diesel fuel and the solid surfaces. These impurities include polar surfactants, heterocyclic aromatics, sulfur and nitrogen compounds which adsorb or react on rubbing surfaces, to reduce adhesion between contacting asperities and thus limit friction, wear and seizure.

The lubricity of diesel fuel vary dramatically. It depends on a wide variety of factors, including the source of crude oil, refining processes and lubricity enhancing additives (alone or in a package with other performance enhancing additives), etc. During 1980s, there was no major lubricity issue associated with the diesel fuel as it used to contain a larger proportion of naturally occurring polar compounds working as lubricity agents. But in 1990s, the refineries were forced to produce highly refined diesel fuel so as to prevent the environment from the polluted gases, thereby bringing low lubricity problem.

3. Reformulated diesel fuels

With the introduction of highly refined diesel fuels, some regulations had also been adopted to reduce emissions and to enable technologies to function effectively with cleaner fuels. The Clean Air Act had been the driving force for these changes, which was first adopted in 1963 and later amended in 1967, 1970, 1977, 1990 [5] and after that also from time to time. In early 1990s, sulfur content of on-highway diesel fuel was reduced from average levels of 0.30% (by weight) to no more than 0.05% (by weight). In 1993, the new standard required a minimum cetane index of 40 or a maximum aromatic content of 35% by volume [6]. Such low sulfur diesel fuels are often called 'reformulated diesel fuels' [7,8] and their production requires severe hydrogenation of some or possibly all the refinery streams to produce the finished fuel.

With the important stiffening of requirements for the quality of diesel fuels, inspite of having different specifications in different countries, a clear trend towards reducing the sulfur content has appeared. In India, the European specifications had limited the percentage of sulfur in diesel fuels to 1% in 1995, which decreased to 0.5% in 1996 and then to 0.05% in 2001. In 2005, the specifications became more stringent to decrease the level of sulfur to 350 ppm (0.035%) (Euro 3) and then to 50 ppm (0.005%) (Euro 4) in 2010. Germany and Sweden has already limited the sulfur in diesel down to 10 ppm (0.001%) (Euro 5). US Environmental Protection Agency (EPA) regulations introduced low sulfur diesel in 1993 with sulfur less than 500 ppm (0.05%), while the new EPA specifications forced the refineries to produce Ultra low sulfur