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Lubricants in the Age of Biodiesel

Abstract

The use of alternative fuels and especially biodiesel is widespread in Western Europe. Biodiesel quickly found its way into the Western European fuels market due to environmental regulations, rising oil prices and political concerns about oil dependence. Most of the diesel sold in Europe now contains some percentage of plant derived fuel. This rapid advance of biodiesel occurred ahead of the understanding of the consequences of biofuel dilution into crankcase lubricant and the resulting effect on the lubricant performance.

In this paper we examine the impact on low temperature pumpability when crankcase lubricants are exposed to biodiesel dilution. The oil drained from a widely used European engine was evaluated after running on various biodiesel fuels, and the concentration and composition of biodiesel in the crankcase as well as soot loading were examined. Our results show that the choice of viscosity modifier (VM) can be crucial to viscometric performance of the oil, both fresh and aged, in vehicles that use biodiesel.

Introduction

Concerns over security of petroleum product supply and the effect of fossil fuel on climate change are driving the use of renewable energy resources. The use of biofuels, including biodiesel, is legislated in several industrialised and developing nations. The term "biodiesel" usually refers to a fuel containing a certain fraction of the plant derived fatty acid methyl esters (FAME), although biodiesel production from animal sources is increasing. In the biodiesel nomenclature, Bxx, B indicates the presence of biologically derived fuel and xx - its percentage. For example, B30 contains 30% of biofuel and 70% of regular diesel; B100 is pure biofuel. The most common plant sources are rapeseed, soy and palm oils that are expected to account for 80% of FAME production globally [1].

Western Europe has the highest demand for biodiesel. Rapeseed, the main local plant source of FAME, does not meet the growing demand. Thus the use of soy and palm methyl esters becomes a reality in Europe together with the small amounts of FAME from the more exotic oilseed sources. Biodiesel as a fuel has similar combustion properties to the petroleum derived diesel, but its chemical composition is different. The chemical composition dictates such properties as fuel cold flow, volatility, and effect on the fuel injection system. Because biodiesel is much less volatile than petroleum derived diesel, it has a tendency to accumulate in a crankcase lubricant when non-combusted fuel gets past the piston rings. This results in lubricant dilution and alteration of its properties. Furthermore, the chemical composition and properties of FAME derived from various plant sources differ significantly. Thus interaction of biodiesel with the crankcase lubricant and in-service properties of this lubricant can depend on the source of biodiesel used. An understanding of the properties of these types of FAME and how they impact lubricant performance is important.

Some work has been done to understand the extent of biodiesel dilution in the lubricants and its effect on oxidation, deposits, wear, corrosion and soot formation [2-10]. The use of biodiesel in general has a negative effect on oxidative stability of the lubricant, deposit formation and corrosion. The use of biodiesel, however, usually results in low soot formation.

In this paper we explore the effect of in-service biodiesel dilution on low temperature pumpability of the crankcase lubricant. We evaluate the oil drained from a widely used European engine after running on bio-fuel and examine the concentration and composition of biodiesel in the crankcase as well as soot loading. We show that the choice of viscosity modifier (VM) can be crucial to viscometric performance of the oil, both fresh and aged, in the engine that uses biodiesel.

Experimental

a. The oils

Similar SAE 5W-40 top tier European oils differing only in the viscosity modifier type were blended for this study in Group III base oil. Three VM chemistries were tested: amorphous hydrogenated styrene-diene star VM (A-Star), semi-crystalline OCP (SC-OCP), and amorphous OCP (A-OCP). Oils were blended to similar kinematic viscosities at 100°C (KV100) and exhibited excellent fresh oil viscometrics (Table 1).

Table 1. *Oils and their viscometric parameters*

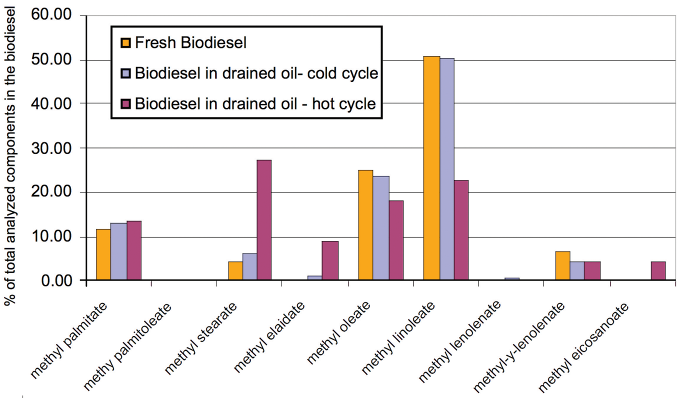
	Oil A	Oil B	Oil C
SAE grade	5W-40	5W-40	5W-40
Detergent Inhibitor (DI) package	11.7	11.7	11.7
VM	A-Star	SC-OCP	A-OCP
Group III base oil	78.3	74.2	75.3
Pour point depressant (PPD)	0.3	0.3	0.3
KV100, cSt	14.0	14.0	13.9
CCS @ -30C, cP	5480	5560	5950
MRV TP-1 app. vis. @ -35C, cP	33700	22600	25300
MRV TP-1 yield stress @ -35C, Pa	<35	<35	<35
HTHS, cP	3.7	3.8	4.0

b. Biodiesel analysis

To quantify the amount of biodiesel dilution and the composition of biodiesel in the crankcase lubricant, the oils were analysed after being subjected to two different service cycles in a widely used European engine run on biodiesel. The amount of FAME was then quantified by FTIR and GC/MS. Both of these analytical methods should be used with caution in quantifying biodiesel dilution in aged oils [11, 12] because of interference from products of lubricant ageing. To validate these techniques, oils aged without the use of biodiesel were diluted with known amounts of fresh biofuel and analysed in a similar fashion. The results showed that the analysis was not significantly affected by ageing by-products. The amount of soy-derived FAME drained from the engine running on B100 in a low temperature service cycle (city driving condition) was in the range of 1.3 to 2.6%. The amount of biodiesel in the oils drained after a high temperature service cycle (highway driving conditions) was between 0.02 and 0.03%.

The GC/MS method was used to analyse biodiesel composition in the drained oils. Only components that were quantified in the fresh biodiesel were quantified in the drained oils. The results (Figure 1) show that the composition of biodiesel in the crankcase lubricant differs significantly with a higher fraction of saturated components versus the fresh biodiesel in the high temperature cycle (hot cycle). The composition of biodiesel in the lubricant running in the low temperature driving cycle (cold cycle) differs only slightly from the fresh biodiesel composition.

Figure 1. *Composition of biodiesel in crankcase lubricant after two different service cycles*



The soot content of the oil can affect viscometric parameters. Multiple studies showed that soot generation is reduced when running on biodiesel [6-9]. Because soot loading is lower than in the case of regular diesel, we did not include soot in our biodiesel dilution experiments.

c. Biodiesel dilution experiments

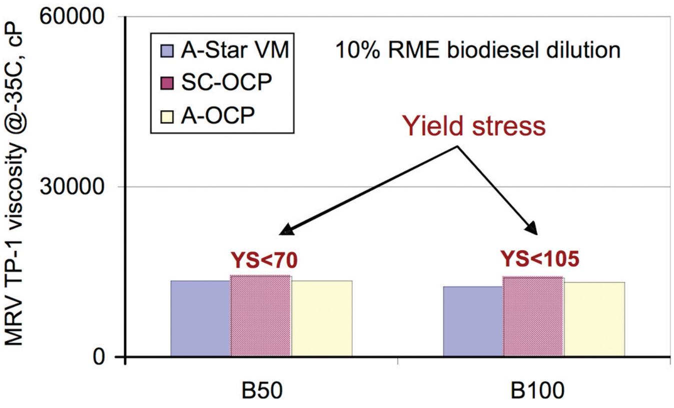
To study the effect of biodiesel dilution on viscometric parameters of the crankcase lubricants and especially on low temperature pumpability, a series of tests was performed. To affect the lubricant viscometrics, a significant amount of biodiesel needs to be present in the crankcase. According to our analysis, this is the case during the lower temperature driving cycle when biodiesel dilution reaches a few percent. Furthermore, our analysis shows that the composition of biodiesel is very close to that of fresh biodiesel in this case. Thus to explore the effect of biodiesel dilution on low temperature viscometrics, we diluted fresh and aged oils formulated with various viscosity modifiers with fresh biodiesel and measured MRV TP-1 apparent viscosity and yield stress of these oils.

Results and Discussion

a. Biodiesel dilution of fresh oils

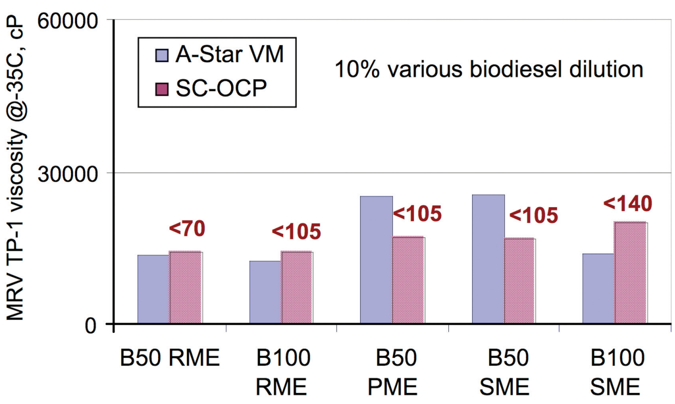
The results of MRV TP-1 tests on three fresh oils formulated with different VMs and diluted with 10% rapeseed-derived biodiesel (RME) B50 and B100 are shown in Figure 2. The MRV TP-1 test measures apparent viscosity of the lubricant, which indicates whether oil will flow upon start-up of the engine, and yield stress. The measurable yield stress indicates that the oil might not flow by itself into the cavity created around the suction tube once the oil that was already in the tube is moved up by the oil pump. If the oil cannot move to the tube, it cannot be pumped to the vital engine parts. The fact that MRV TP-1 yield stress causes lack of pressure build-up and, therefore, lack of lubrication oil in the vital engine parts upon start-up, has been demonstrated in the vehicles [13]. Figure 2 shows that dilution with both B50 and B100 RME fuel results in yield stress in the oil formulated with semi-crystalline OCP. The measured yield stress is indicated in the same color as the bar showing the value of apparent viscosity measured in the MRV TP-1 test. Both oils formulated with amorphous VMs (A-Star and A-OCP) can tolerate RME biodiesel dilution without developing a yield stress.

Figure 2. *MRV TP-1 performance of three fresh oils diluted with rapeseed oil based biodiesel (RME). Patterned bars indicate the presence of yield stress. Yield stress value in Pa is shown in the same color next to the bar indicating the apparent viscosity value.*



MRV TP-1 response to dilution of oils formulated with amorphous VM (Star A) and semi-crystalline VM (SC-OCP) with biodiesel of various sources (rapeseed oil methyl ester – RME, palm oil methyl ester – PME, and soy oil methyl ester – SME) is shown in Figure 3. In all cases, oils formulated with SC-OCP developed yield stress upon biodiesel dilution. The SC-OCP oil diluted with B100 PME did not yield to the highest stress applied resulting in solid-like behavior (not shown in the Figure for this reason).

Figure 3. *Comparison of MRV TP-1 responses of oils with amorphous and semi-crystalline VM upon dilution with various types of biodiesel. Patterned bars indicate the presence of yield stress. Yield stress value in Pa is shown in the same color next to the bar indicating the apparent viscosity value.*



This study demonstrates that the choice of the VM in otherwise similar oils can be crucial to viscometric performance of the oil in the engine that runs on biodiesel.

b. Biodiesel dilution of aged oils

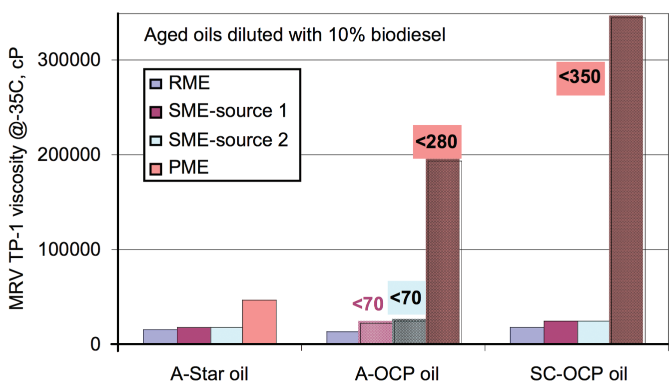
To study the effect of biodiesel dilution throughout the lifetime of the lubricant, biodiesel was added to the oils aged without the presence of biodiesel. For this study a different semi-crystalline OCP was used, and the pour point depressant (PPD) was optimized for biodiesel application in this oil (Oil B-PPD2) while all the other components remained the same. This approach was taken because the interactions already present in the fresh oil diluted with biodiesel and causing MRV TP-1 failure could overshadow any ageing effect. Fresh Oil B-PPD2 responded well to biodiesel dilution with passing MRV TP-1 results in the same dilution experiments as demonstrated in Figure 3. The MRV TP-1 results for the oils aged without biodiesel present are shown in Table 2. All aged oils have passing MRV TP-1 results.

Table 2. *MRV TP-1 results for similar aged oils with three different VMs.*

	Oil A	Oil B-PPD2	Oil C
VM	A- Star	SC-OCP	A-OCP
MRV TP-1 app.vis @ -35C, cP	34955	37758	26346
MRV TP-1 yield stress @ -35C, Pa	< 35	< 35	< 35

The biodiesel dilution of these aged oils is shown in Figure 4. Both amorphous OCP and SC-OCP aged oils exhibit high yield stress upon dilution with PME. It is not surprising that PME is the most severe type of biodiesel for low temperature performance, because it contains the highest fraction of saturated components that tend to form crystals. The catastrophic MRV TP-1 failure of SC-OCP oil is most likely due to facilitation of crystal formation and growth by the VM. On the other hand, the aged oil formulated with amorphous star VM tolerates dilution by biodiesel of any plant source providing excellent performance in any biodiesel application.

Figure 4. *MRV TP-1 result comparison for aged oils formulated with different VM and diluted with biodiesel. Patterned bars indicate the presence of yield stress. Yield stress value in Pa is shown in the same color next to the bar indicating the apparent viscosity value.*



Conclusions

We examined the impact of biodiesel exposure on low temperature pumpability of crankcase lubricants. In particular the effect of biodiesel interaction with various viscosity modifiers in fresh and aged oils was studied. We reached the following conclusions:

- High biodiesel dilution occurs during city driving (cold cycle) conditions.
- Biodiesel dilution is a few percent in this driving regime.
- Composition of biodiesel in the oil during city driving cycles (low temperature conditions) is close to that of fresh biodiesel.
- These conditions can be simulated by diluting fresh or aged oil with fresh biodiesel.
- Dilution experiments showed that biodiesel components can interact with lubricant components, especially VM, in both fresh and aged oils and cause low temperature pumpability failure (MRV TP-1 failure) of the lubricant. Semi-crystalline OCP VM is more prone to these interactions and resulting failures, while amorphous VMs offer better performance in biodiesel applications. Amorphous styrene-diene star VM offers the most robust performance in biodiesel applications across a wide range of plant sources.

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