EFFECT OF C_{60} ON OXIDATIVE STABILITY OF FUELS

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ABSTRACT

Prompted by the ability of fullerenes to intercept radical chain processes, we investigated their possible application as additives to enhance thermal and storage stabilities of fuels. The thermal stability was evaluated using a gravimetric JFTOT apparatus, and the storage stability was assesses using the oxygen overpressure test. At a doping of 24 ppm, we found a significant beneficial effect of C_{60} in enhancing the thermal stability of jet fuels, but only a marginal effect for the storage stability of diesel fuels. In addition, we found that the presence of fullerenes had no effect on hydroperoxide formation as long as the fuel was kept in the dark. However, exposure to ambient light led to the build up of substantial quantities of hydroperoxides.

INTRODUCTION

Formation of insolubles in the fuel is a general problem. It can happen under various conditions, such as thermal stressing of jet fuels at 250 - 400°C during a flight, or during long term (years) storage of diesels under ambient conditions (10 - 45°C). The formation of insoluble materials can lead to many problems such as plugging of filters or fouling of engine parts.[1,2] In the extreme case when fuel flow is completely blocked, the consequence is extremely serious. Autoxidation has been implicated as a key step in the chemical scheme resulting in insolubles formation. This process involves generation of radical species, which initiate a chain reaction with oxygen to give oxidized hydrocarbons. The scheme, as originally proposed by Hazlett, is shown below:

INITIATION:

$$R\text{-}H + X \;(\text{metal ion or surface}) \rightarrow R\bullet + XH$$

PROPAGATION:

$$R\bullet + O_2 \rightarrow ROO\bullet$$

$$ROO\bullet + R\text{-}H \rightarrow ROOH + R\bullet$$

TERMINATION:

$$ROO\bullet + ROO\bullet \rightarrow ROH + R'COR'' + O_2$$

$$ROO\bullet + R\bullet \rightarrow ROOR$$

$$R\bullet + R\bullet \rightarrow R\text{-}R$$

In view of the ability of C_{60} to scavenge radicals[3] we decided to test the effect it would have on (i) thermal stability of jet fuels, (ii) storage stability of diesels, and (iii) hydroperoxide formation.

RESULTS AND DISCUSSION

Numerous studies have been conducted on the chemistry leading to insolubles formation in jet fuels at elevated temperatures.[1] Key reactions are the thermal decomposition of alkyl chains by the Rice Herzfeld mechanism and autoxidation. The thermal stability tests were conducted using a gravimetric JFTOT apparatus with two JP-5 fuels (J1 and J2) and commercial Jet A fuel (JA). The JFTOT strip was heated to 260°C and 450 mL of fuels were pumped over it at 3.0 mL/min. The weight of the deposits on the strip as well as those collected on the filter were determined. The strip deposit is often very small (about 5-10%) of the total deposit. However, addition of 24 ppm C_{60} reduced deposit formation on the strip as well as the filtered deposit by about 50%. The data for the total deposits are displayed in Figure 1. The reduction in the fuel J1, which had a commercial additive package in it, is particularly noteworthy, because C_{60} was able to further reduce the very small amount of the deposit. An additive-free jet fuel (J2), which gave 15 mg/L of deposits, gave only 5.5 mg/L when doped with 24 ppm C_{60}. Finally, a commercial jet fuel, Jet A, which also had the additive package in it, showed no beneficial effect upon doping with C_{60}.

The chemistry of insolubles formation during long term storage is fairly complex and involves many different reactions. A possible scenario includes oxidation of sulfur species to sulfonic acids which catalyze the nucleophilic reaction of alkylindoles with phenalenones, which are also formed by autoxidation.[4] Tests on the storage stability of diesels were conducted with two diesel fuels (D1 and D2) by the oxygen over pressure (oop) test developed at the Naval Research Laboratory.[5] Both of the fuels are a 20% light cycle oil blend with the straight run diesel. The fuels were stressed for 16 h at 90°C with 100 psig O_2. The results are shown in Table 1.

Table 1. Effect of C_{60} on the insolubles formation in diesel fuels during the oxygen overpressure test (90°C, 16 h, 100 psig O_2)

Fuel ID	Neat	+24 ppm C_{60}	% Redn.
DI	56	47	16
D2	44	34	23

At the doping level of 24 ppm both fuels responded to the addition of C_{60}, although the more unstable fuel, Fuel D1, exhibited a modest 16% reduction deposit formation. At a similar level of doping with an alkyl amine additive, these fuels showed a reduction in deposit formation of about 70%. Thus, C_{60} is not a particularly effective agent for enhancing the storage stability of diesel fuels.

Finally development of hydroperoxides in an unstable JP-5 fuel, held in the dark at 102°C under 50 psia air, was monitored over a 150-h duration. The results are illustrated in Figure 2. Initially, C_{60} (@24 ppm) accelerated the hydroperoxide formation, but at the end (~140 hr), both samples—additive free and doped—show the same low values. Experiments were also conducted with a stable JP-5 at ambient temperatures under a fluorescent light in the presence of 0, 5, 10, and 20 ppm C_{60}. In control experiments, there was no formation of hydroperoxides in the dark, but C_{60} had a profound influence on the formation of hydroperoxides in the light. These results further illustrate the ability of C_{60} to photosensitize the oxidation of other substrates.

These preliminary data show that although C_{60} reduces the deposit formation in jet fuels, it can also have deleterious effects, particularly if the fuel were to be exposed to light. Further work with functionalized fullerenes is currently under way.

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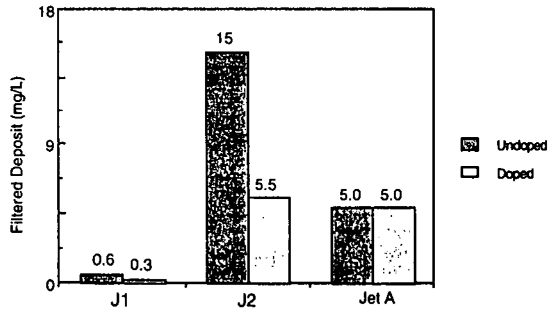

FUELS

J1: JP5 (contains additives)
J2: Fresh blend (unstable)
Jet A: Commercial aviation fuel (contains eddilives)

Doping at 24 mg/L

Figure 1. Effect of C_{60} on the thermal stability of jet fuels as determined in a gravimetric JFTOT test conducted at 260°C.

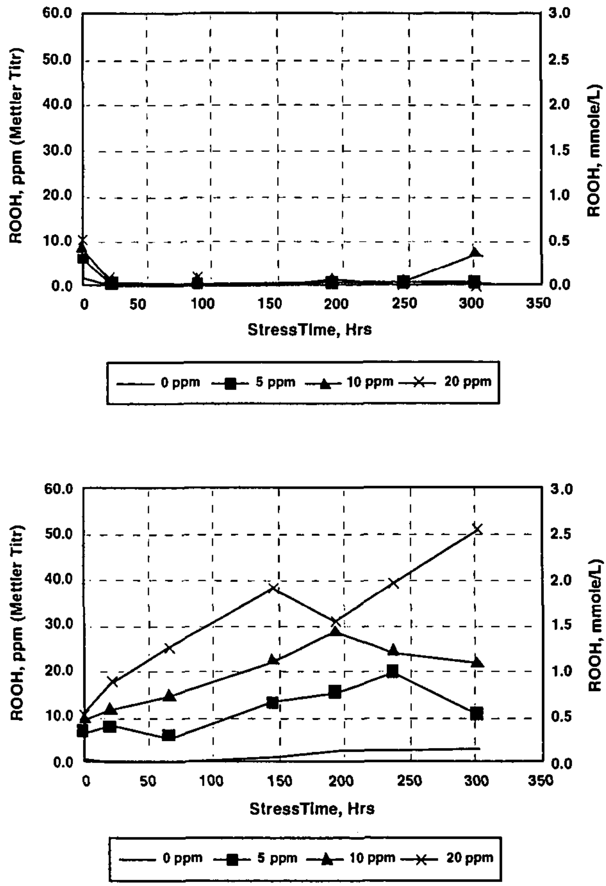

Figure 2. Effect of C_{60} on the peroxide formation at 25°C in aviation fuel 91-7 in (a) dark and (b) in light.