Significant Reduction of Carbon Deposit by Hydrogen Donor Addition to JP-8 Jet Fuel at High Temperatures

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Introduction

Advanced high-Mach aircraft will require the fuel to perform a dual role as a coolant for mechanical and electrical systems in addition to serving as the propellant, thus increasing the thermal stability requirements of the fuel[1]. The conventional paraffin-based fuels have poor thermal stability due to the high susceptibility of the paraffinic components to free radical reactions[2]. Uncontrolled radical reactions will lead to fuel decomposition which ultimately leads to carbonaceous deposit formation in both the bulk of the fuel and on the surfaces of various fuel system components.

Previous work conducted at Penn State has shown hydrogen donors such as tetralin can help control such radical reactions reducing carbon formation from the pyrolytic degradation of paraffinic fuels[3]. In the presence of dissolved oxygen, traditional hydrogen donors can undergo autoxidative reactions, resulting in retardation of the donor's effectiveness in the pyrolytic regime. Recently, a binary donor consisting of a 1:1 blend of tetralin and α-tetralone has shown excellent oxidative resistance while reducing the formation of polyaromatics and subsequent carbon formation[4,5].

The effect of the trace amount of some sulfur compounds appears to be significant on the rate of deposit formation and metal surface degradation. Taylor[6] examined the role of sulfur compounds in deposit formation for a JP-5. Selected compounds were added in amounts to give a sulfur concentration in the fuel of 3000 ppm. Diphenyl sulfide (DPS) and phenyl benzyl sulfide (PBS) were added to JP-5 fuel and it was observed that both sulfur compounds enhanced the deposition throughout the temperature range with maxima occurring in the 427 to 482˚C range, but phenyl benzyl sulphide exerted much more significant effect. Polysulfides, disulfides, thiol, and other sulfides increased deposition dramatically. On the other hand, benzothiophene and diphenzothiophene did not contribute to the formation of deposits. Increasing the level from 300 to 3000 ppm approximately doubled the amount of deposits with both DPS and PBS compounds.

This study aims at further understanding the role of hydrogen donors on the formation of solid carbons d during thermal stressing of jet fuel through examination of the morphology and reactivity of the deposits from JP-8 stressed with the addition of various concentrations of tetralin and a binary donor of tetralin and α-tetralone

Experimental

Thermal stressing of JP-8 fuels was performed in the presence of Inconel 600 foils, the elemental composition of which is listed in Table 1. For each experiment a foil having approximate dimensions of 100 x 3 x 0.1 mm was placed at the bottom of a 1/4" o.d. isothermal flow reactor lined with a glass coating developed by Alltech Corporation. Prior to inducing the fuel into the system, the reactor was heated to 500°C wall temperature under argon flow at 500 psig.

Table 1. Elemental Composition of Inconel 600

Ni, %	Fe, %	Cr, %	Mn, %	Cu, ppm	C, ppm	Si, ppm	S, ppm
72	8	15.5	1.0	5000	1500	5000	150

The hydrogen donors used in this study was tetralin and a binary donor of 1:1 mixture of tetralin and α-tetralone, which was added to JP-8 in varying concentrations. The fuel was pre-heated to 200°C before entering the reactor, which was held at a constant 475°C bulk fuel outlet temperature. Pressure was maintained at 500 psig throughout each experiment. Each experiment was conducted for 5 hours with 4mL/min flow of fresh fuel.

Carbon deposits on the metal foils were analyzed by temperature programmed oxidation (TPO) using a LECO R412 Multiphase Carbon Analyzer to determine the total amount of carbon on the surface in μg of carbon per square centimeter (μgC/cm^2). Morphology of the deposits was characterized by a Hitachi S-3500N scanning electron microscope (SEM).

Results and Discussion

Tetralin addition. Figure 1 shows the TPO profiles of carbon deposits detected from thermal stressing of JP-8 with and without tetralin additions of 1, 2, 5 and 10 vol.%. Without any tetralin addition, JP-8 produced 25.7 μgC/cm^2 on the Inconel 600 foil. With only 1% addition of tetralin the total amount of carbon is reduced by nearly 46% to 14.2 μgC/cm^2. Further increasing the tetralin content to 2 and 5% further reduced the amount of carbon by 81.3%. Above 5% tetralin addition, the total amount of carbon produced on the foils began to increase slightly from 4.8 to 5.7 μgC/cm^2 with 5 and 10% tetralin addition, respectively.

The SEM images of the foils without tetralin addition are presented in Figure 3. The surface shows near complete coverage by metal sulfides (NiS, FeS) and filamentous carbon with regions of amorphous carbon. With the addition of 2 and 5% tetralin the carbon formed on the surface is significantly reduced, as shown in the SEM images in Figure 4. The addition of tetralin also shows nearly no filament formation on the surface whereas some needle-like metal sulfide formations are apparent. By combining the TPO and SEM analysis, we see that peak III of the TPO analysis is significantly reduced with the addition of tetralin, thus indicating that peak III can be attributed to catalytically initiated filamentous carbon on the surface. Although filamentous carbon is nearly eliminated with tetralin addition greater than 2%, there still are regions of amorphous deposits, which correspond to peak II of the TPO profiles.

It appears shows that the formation of sulfides on the surface is also significantly reduced upon tetralin addition, as implied by SEM analysis. Previous studies have shown that

certain sulfur compounds, such as biphenylsulfide (BPS) will increase carbon deposition while other sulfur compounds such as thiophene and benzothiophene can reduce carbon formation[7,8]. Altin and coworkers concluded that some organo-sulfur compounds such as BPS will facilitate the formation of Ni and Fe sulfides, which in turn will increase carbon deposition due to the formation of high surface area which increases the retention time of reactive hydrocarbon molecules on metal substrate to decompose further. The upward growth of metal sulfide crystals produces nano metal particles which accelerate the filamentous carbon deposits. From the decrease in the formation of sulfides when tetralin is added to the JP-8, it is concluded that tetralin is aiding in stabilizing the reactive sulfur species which lead to the formation of sulfides and subsequent carbide formation, thus reducing the formation of filamentous carbon on the surface.

Binary donor addition. TPO analysis of the Inconel 600 foils after thermal stressing of JP-8 with 1, 2 and 5 vol.% addition of a 1:1 mixture of tetralin and tetralone is presented in Figure 2. Similar to tetralin addition, there is a reduction in carbon deposits by nearly 50% with only 1% addition of the binary donor. Further addition of the binary donor further reduced the total amount of carbon formed on the surface of the foil. However the degree of carbon reduction of the binary donor is not as high as that of only tetralin addition.

SEM examination shows that even with 5 vol.% addition of the binary donor to the JP-8, there is significant filamentous carbon formation with a larger reduction in amorphous deposits. With the addition of the binary donor, there is still significant formation of sulfides on the surface.

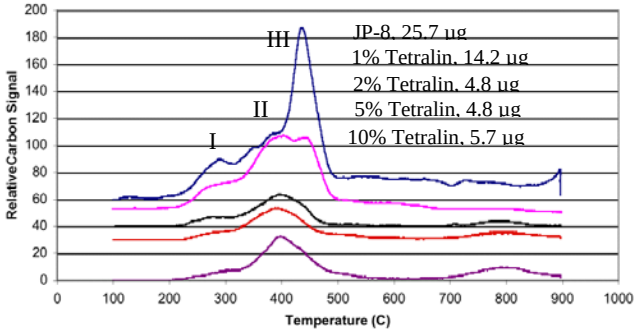

Figure 1. Effect of tetralin addition to JP-8 deposit formation from thermal decomposition at 475°C for 5 hours as analyzed by TPO.

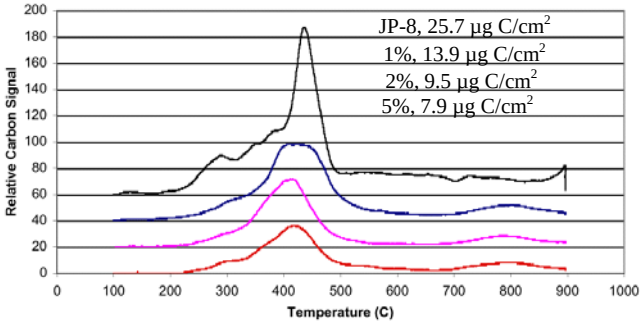

Figure 2. Effect of a binary donor comprised of a 1:1 mixture of tetralin and tetralone to JP-8 deposit formation from thermal decomposition at 475°C for 5 hours as analyzed by TPO.

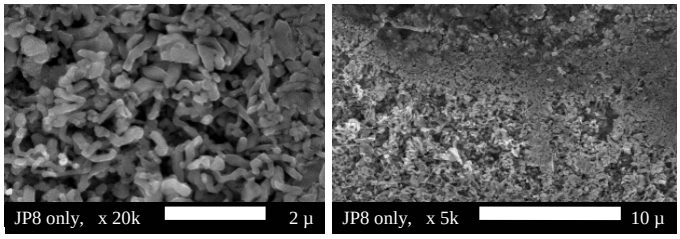

Figure 3. SEM imaging of the Inconel 600 surface after 5 hours of thermal stressing of JP-8 only at 475°C (magnification at 20k and 5k).

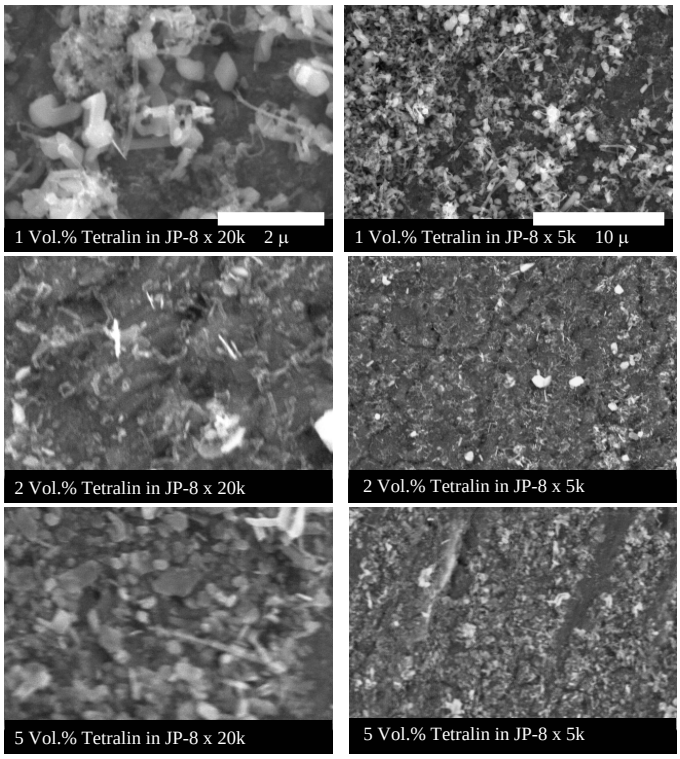

Figure 4. SEM imaging of the Inconel 600 surface after 5 hours of thermal stressing of JP-8 with 1, 2 and 5 vol.% tetralin addition at 475°C (magnification at 20k and 5k).

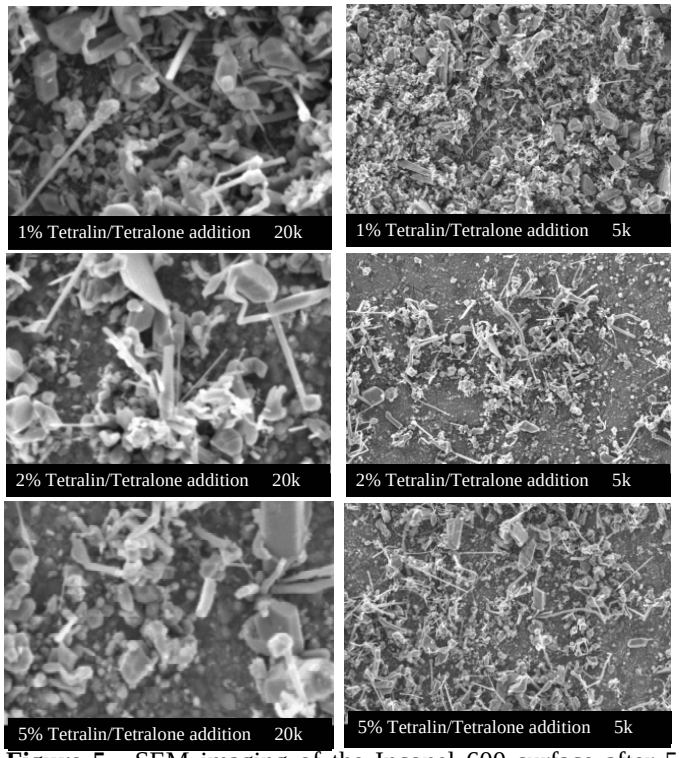

Figure 5. SEM imaging of the Inconel 600 surface after 5 hours of thermal stressing at 475°C of JP-8 with 1, 2 and 5 vol.% of a binary donor of tetralin and tetralone (magnification at 20k and 5k).

Conclusions

Addition of only 2 vol.% tetralin to JP-8 jet fuel showed a significant reduction in carbon deposit accumulation on the surface by over 81% when compared to JP-8 without any additives. The carbon deposition that resulted from pyrolytic stressing of JP-8 with tetralin addition is mainly amorphous carbon with little presence of filamentous carbon and sulfide formation. Tetralin has the ability not only to help prevent bulk deposits, but is able to stabilize the organic sulfur compounds present in JP-8. By the reduction of sulfide formation, amorphous and filamentous carbon formations are significantly reduced.

The addition of up to 5 vol.% of a binary donor, which is comprised of a 1:1 mixture of tetralin and tetralone, lower degree of reduction in amorphous carbon is observed. This implies that although previous work as shown that the binary donor is more effective in reducing the bulk deposits associated with the formation of polyaromatics, the binary donor is not able to reduce the filamentous carbon. Sulfide formation was also significant from the decomposition of organic sulfur compounds in the JP-8 even with binary donor additions. The decomposition of the sulfur compounds present in the JP-8 fuel leads to the formation of amorphous and filamentous carbon growth. The filaments present on the surface with the addition of the binary donor are longer and thinner than the filaments observed with JP-8 only. This implies that the binary donor is reducing the levels of polyaromatics and bulk deposits, thus the metal sites that are active for the growth of such filaments remain active since they are not being encapsulated by carbon, as is the case when no additive is added to JP-8.

Acknowledgement. We are grateful for financial support from the U.S. Air Force Office of Scientific Research. We thank Mr. Jean-Philippe Alphonse Kouassi for his help with the experiments.

References

(1) Edwards, T. and Zabarnick, S. *Ind. Eng. Chem. Res.* **1993**, 32, 3117.
(2) Song, C.; Eser, S.; Schobert, H.H.; Hatcher, P.G. *Energy & Fuels* **1993**, *7*, 234-243.
(3) Song, C.; Lai, W.-C.; Schobert, H.H. *Ind. Eng. Chem. Res.* **1994,** *33*, 548.
(4) Strohm, J.J.; Andresen, J.M.; Song, C. *Prepr. Pap. – Am. Chem. Soc., Div. Fuel Chem.*, **2002**, *47*(3), 189.
(5) Strohm, J.J.; Brandt, A.J.; Eser, S.; Song, C. *Prepr. Pap. – Am. Chem. Soc., Div. Fuel Chem.* **2003**, *48*(2), 857.
(6) Taylor, W. F., *Ind. Eng. Chem. Prod. Res. Dev.* **1976**, 15, 64.
(7) Altin, O., Raymundo-Pinero, E., Eser, S., *Proceedings, Carbon 2002, International Carbon Conference*, Paper # E038, CD, **2002**..
(8) Raymundo, E.; Altin, O.; Eser, S. *Prepr. Pap. – Am. Chem. Soc., Div. Pet. Chem.* **2002**, 47(3), 216.