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Introduction

In the future, jet fuel used by high-Mach aircraft will be expected to perform a dual role as a coolant for mechanical and electrical systems, raising temperatures experienced by the fuel to greater than 480°C.¹ Current jet fuels are derived from petroleum sources resulting in a predominately paraffinic fuel. At these temperatures, linear paraffins are highly susceptible to pyrolytic degradation leading to the formation of carbon deposits² on metal surfaces within the aircraft through bulk and/or catalytic reactions. Bulk deposits that are formed are generally due to the condensation of alkyl benzenes either present in the fuel or formed from pyrolytic dehydrogenation reactions, which results in deposits that have a general structure of 6 to 7 aromatic rings.³ Previous work has shown hydrogen donors such as tetralin and α-tetralone can reduce such pyrolytic reactions under non-oxidative conditions, thus effectively reducing the formation of bulk deposits.⁴ The presence of dissolved oxygen in the fuel dramatically lowers the effectiveness of such hydrogen donors in the pyrolytic regime, rendering them useless.⁵ Recently, a binary hydrogen donor consisting of α-tetralone and tetralin has shown excellent oxidative resistance while significantly preventing the formation of polyaromatics.⁶,⁷

Catalytic deposition is associated with adsorption and subsequent reactions on metal surfaces resulting in filament or amorphous carbon growth. Composition of the metal surface has a profound effect on the formation rate and structure of deposits.⁸,⁹ Superalloys based on the group VIIIA elements were developed for high-temperature applications in corrosive environments, and have been used successfully in aircraft parts and nuclear reactors.¹⁰ However, these alloys still contain Ni and Fe, which are known to catalyze the growth of carbon filaments.¹¹

The current study seeks to investigate the effect of the previously developed binary hydrogen donor on the morphology of carbon deposits formed on the superalloy, Inconel 718, during stressing of JP-8 under pyrolytic conditions while dissolved oxygen is present in the fuel.

Experimental

Thermal stressing of JP-8 fuels was performed in the presence of Inconel 718 foils, whose elemental composition is listed in Table 1. For each experiment a foil having dimensions of 10 x 3 x 0.1 mm was placed at the bottom of a 1/4” o.d. isothermal flow reactor, lined with a Silcosteel coating developed by Restek Corporation. Prior to introducing fuel into the system, the reactor was heated to 500°C wall temperature under argon flow at 50 psig.

Table 1. Elemental Composition of Inconel 718a,b

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb+Ta</td>
<td>5000</td>
<td>19%</td>
<td>1500</td>
<td>18.5%</td>
<td>1800</td>
<td>3.05%</td>
</tr>
<tr>
<td>Ni</td>
<td>5.13%</td>
<td>52.5%</td>
<td>1800</td>
<td>9000</td>
<td>400</td>
<td>80</td>
</tr>
</tbody>
</table>

aFrom Goodfellow Co. and expressed in weight percent. bAl, Cu, Mn, Si, Ti, C and S in ppm.

The fuels used in this study were 1 L of JP-8 with and without a 2 wt% addition of the binary hydrogen donor consisting of equal amounts of α-tetralone (THNone) and tetralin (THN). Each fuel was circulated through the reactor at a rate of 4 mL/min for a period of 24 hrs. The fuel was heated to 200°C before entering the reactor, and the bulk outlet temperature of the fuel was maintained at 500°C. Pressure was held constant at 500 psig, and liquid fuel samples were taken at six-hour intervals.

Carbon deposits on the metal foils were analyzed using a LECO R412 Carbon Analyzer to determine total amounts of carbon on the surface in μg/cm². Morphology of deposits was characterized by a Hitachi S-3500N scanning electron microscope. A Shimadzu GC-174 gas chromatograph with a Restek Xti-5 column coupled to a Shimadzu QP-5000 mass spectrometer was used to examine liquid samples. Solution state ¹³C-NMR analysis was conducted on a Bruker AMX360 with a field of 8.4 T equivalent to a 90 MHz resonance frequency for ¹³C. Approximately 0.2 mL of sample was diluted in 1 mL CDCl₃ and charged into a 5 mm tube. A pulse delay of 90 seconds was required to obtain a quantitative spectrum.

Results and Discussion

Impact on Fuel Reactions. Previous investigations of binary hydrogen donors have shown large improvements in preventing pyrolytic reactions leading to polyaromatic formation and bulk deposits. In a separate flow reactor system JP-8 was stressed with and without the binary hydrogen donor added to the fuel. Silcosteel was used to passivate the surface, in order to minimize catalytic decomposition of the fuel. The reactor utilized higher space velocities, leading to higher temperature conversions, which allowed direct examination of fuel and hydrogen donor interactions. Figure 1 shows the impact of the binary hydrogen donor on the final fuel composition when the fuel was stressed up to a bulk outlet temperature of 772°C (with a LHSV = 450 hr⁻¹).

Figure 1. Impact of a binary hydrogen donor on the stabilization of pyrolytic reactions leading to the formation of PAHs as illustrated by ¹³C-NMR analysis of the stressed fuels.¹²

As Figure 1 illustrates, there is a clear increase in the prevention of the total aromatic carbon that is formed when the binary hydrogen donor is added (32% reduction). More significantly, there is a 62% reduction in the formation of bridgehead carbon associated with PAH formation. In the base of the aliphatic region of the spectra, there is

an increased broadening indicating increased cyclization of the initial fuel. Overall, the signature of the JP-8 remains more intact upon stressing when the hydrogen donors are added to the fuel; clearly this indicates a decrease in the decomposition of the fuel, and subsequent formation of precursors to bulk deposits.

**Impact on Carbon Formation.** TPO investigation of carbon produced on the surface of the Inconel 718 foils showed no difference in the total amount of carbon produced when the binary hydrogen donor was added to the JP-8. The TPO profiles, however, indicated that carbon produced when the hydrogen donor was added were indeed different from the carbon produced in its absence. To further examine the morphology of the carbon produced, SEM analysis was conducted and is presented in Figure 2.

With the addition of the binary hydrogen donor to JP-8, there is enhanced formation of filamentous carbon when compared to the stressing of JP-8 only. Previous work has shown

![Figure 2](image1.png)

Figure 2. Scanning Electron Micrographs of deposits on the surface of Inconel 718 after thermal stressing for 24 hrs in the presence of JP-8 with (top) and without (bottom) hydrogen donors.

that filamentous carbon is due to catalytic reactions of metals such as nickel and iron with reactive species from thermal decomposition of the fuel.\(^2\) Research in the field of steam reforming of hydrocarbons over nickel catalyst have shown that filament growth is due to the adsorption and diffusion of carbon through nickel particles.\(^3\) When the particles of nickel are encapsulated by polymeric carbon, the activity (and growth of the filaments) is reduced. A similar explanation is given here for the observed differences in the carbon produced from the thermal stressing of JP-8 with and without hydrogen donor addition.

Stressing of JP-8 without the hydrogen donor shows very short and fat carbon filaments with regions of highly amorphous carbon. It is proposed that the reason for the short filaments and amorphous carbon is due to the lay-down of polyaromatics on the surface. This lay-down of polyaromatics will terminate the catalytic activity of active metals such as nickel, resulting in the termination of filament growth. In addition, the initial lay-down of polyaromatics will facilitate an increase in amorphous deposits, due to increasing condensation and dehydrogenation reactions propagating on the surface that is already coated with amorphous deposits. This also accounts for the “regions” rather than irregular coverage of amorphous carbon that was observed on the surface when hydrogen donor is added to the fuel.

![Figure 3](image2.png)

Figure 3. Scanning Electron Micrographs using secondary electrons (top) and back-scattered electrons (bottom) of deposits on the surface of Inconel 718 after thermal stressing for 24 hrs in the presence of JP-8 plus a 1% mixture of α-tetralone and tetralin.

Without the encapsulation of the active metal particles by polyaromatic lay-down, or by active hydrocarbon species from the degradation of the fuel polymerizing, the filaments can continue to grow. This is the case that is observed when hydrogen donors are added to the fuel. The decrease in the formation of polyaromatics, and the suppression of radical reactions that serve to enhance carbon

deposition prevent the encapsulation of active metals, thus allowing enhanced filament growth.

To confirm that metal species were present at the tips of the filaments that were growing, back-scattered electron (BSE) images from SEM analysis were investigated. Figure 3 shows a typical SEM image (top) of the surface after stressing of JP-8 with hydrogen donor addition and the corresponding BSE image of the same area. The light areas of the BSE image correspond to heavy elements that are present on the surface. It is seen that the ends of some of the filaments observed from the SEM image have light areas associated with them in the BSE image. Since the only heavy elements that would be present in the system would be metals, it is shown that these filaments do have metals located near their tips. Not all of the filaments show light areas near their tips, and this is due to some of the filaments being encapsulated by carbon, thus terminating the filament growth as seen in the SEM image of Figure 3.

Conclusions

The effect on the morphology of carbon produced from thermal stressing of JP-8 over Inconel 718 after adding a binary hydrogen donor, comprised of tetralin and α-tetralone, has been examined. Hydrogen donor addition can significantly improve the detrimental pyrolytic reactions leading to the formation of polyaromatics and other reactive species, which results in the formation of bulk and amorphous deposits on the surface. However, the reductions of such compounds being formed will allow the enhanced formation of filamentous carbon. The enhanced production of filamentous carbon is caused by the metal particles on the tips of the filaments remaining active, since they are not being encapsulated by pyrolytic carbon. To effectively reduce the formation of carbon during the pyrolytic decomposition of paraffinic-based fuels, a dual approach to the problem is needed. The first step is to passivate the surface so that the metals, such as nickel that can lead to filamentous carbon, do not interact with the fuel. Secondly, to eliminate the formation of amorphous carbon from bulk reactions, hydrogen donors can be added to the fuel to reduce the formation of polyaromatics, which are the precursors to the formation of amorphous carbon.

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References