DEPOSIT FORMATION CAUSED BY THERMAL STRESSING OF PETROLEUM AND COAL-DERIVED JET FUELS ON INCONEL 718 AND FUEL PRE-TREATMENT EFFECT

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Introduction

Jet fuel is presently used as a coolant in military aircraft, in addition to its primary use as a propellant. It is used to cool the lubrication system, avionics, electrical systems, and environmental control systems, and is also used as a hydraulic fluid (1). The trend of advanced aircraft toward increasing performance results in the formation of carbon deposits on the metal cooling line surfaces. The buildup of deposits in aircraft fuel systems is a major concern because of resulting possibility of fuel system failure. To achieve optimal performance capabilities for the next generation of jet engines, significant improvement in jet fuel thermal stability is necessary. This objective has led Penn State University and U. S. Air Force to initiate a program to develop a jet fuel that would be thermally stable up to 480˚C (900˚F). Napthene-rich coal derived jet fuels have been shown to be more thermally stable than their petroleum-derived counterparts. The thermal stability requirements of these advanced fuels indicate the types of hydrocarbons and potential additives that may be present in advanced fuels (2,3). Exposure of metallic surfaces to jet fuels at temperatures higher than 400˚C lead to carbonaceous deposits (4-6). Various metallic alloy candidates were examined at Penn State to observe their catalytic activity in carbon deposit formation from jet fuel decomposition and found that Inconel X and Inconel 718 collected significantly less amount of deposit at 500 and 600 ˚C during jet fuel stressing experiments (7-8). The sulfur level and type of sulfur compounds present in the jet fuel are also crucial parameters from the surface catalytic effect point of view. It was found that sulfur compounds decomposed to form elemental sulfur which has high tendency to react with the alloying elements of metal surface resulting severe surface corrosion (9-10).

Hydroperoxides and peroxides are early precursors in the oxidative degradation of hydrocarbons. Activated alumina is effective in destroying organic peroxides and hydroperoxides present in organic samples. In earlier preliminary work (11), it was found that a small amount of alumina added to a sample, and then rempved by filtration just prior to thermal treatment of jet fuel, resulted in less color change and essentially no carbonaceous deposit formation under conditions that produced significant quantities of deposit in darkly colored products. These earlier studies prompted the experiments described herein.

This study examines the thermal stability behavior of 1:1 and 3:1 blends of hydrotreated refined chemical oil (HDT-RCO with hydroterated light cycle oil (HDT-LCO), and JP-8 on Inconel 718 surface at 500˚C of fuel temperature in terms of carbon deposit amount and microscopic deposit morphology.

Experimental

The fuels tested in the thermal stressing experiments on Inconel 718 are coal-based blends (1:1 vol) HDT-RCO/HDT-LCO), (3:1 vol) HDT-RCO/HDT-LCO), and petroleum-based JP-8. None of the jet fuel range materials contained additives. The nominal composition of Inconel 718 alloy is (wt%) Ni: 52.5, Fe:18.5, Cr:19, Mo:3.05, Al:0.5, Ti:0.9, Nb+Ta:5.13, Cu:0.15, Mn:0.18, Si:0.18, C:0.04, S:0.0008. The alloy foils, 15 cm x 3 mm x 0.6 mm, were cut and rinsed in acetone. Thermal stressing of fuels was carried out at 470˚C fuel temperature (525˚C wall temperature) and 250 psig (17 atm), 500 psig (34 atm) and 900 psig (61 atm) in the presence of Inconel 718 alloy foil. The fuel was subjected to stressing for 5 hr at a 4 ml/min flow rate. The alloy foil was placed in the 20 cm and 1/4 in OD glass lined stainless steel tube reactor. Chemical composition of jet fuels was determined by using GC/MS analysis. Sulfur content of the jet fuels was measured by using GC/PFPD. The total amount of carbon deposition on metal coupons was determined using a LECO Multiphase Carbon Analyzer. The deposits formed on Inconel 718 surface were characterized by temperature-programmed oxidation (TPO), Field Emission SEM, and energy-dispersive spectroscopy (EDS).

Results and Discussion

Carbon Deposit Analysis - Thermal stressing of petroleum-derived, and coal/petroleum blended fuels in the presence of Inconel 718 has been shown to produce a wide range of carbon deposit amounts (12). Carbon deposit amounts are given in terms of µg C per cm^2 of Inconel 718 alloy.

In this study, as a result of reaction at 500˚C and 250 psig, jet fuel consisting of a hydrotreated mixture of 3:1 RCO/LCO (as received) produced higher levels of carbon deposit (33.7µgC/cm^2) than a hydrotreated mixture of 1:1 RCO/LCO (as received) (9.8µgC/cm^2) (Table 1). In this report, as received is meant to be hydrotreated product, stored in the presence of air. At 500 psig under similar conditions, the 3:1and 1:1 fuels gave 3.9 and 3.6µg/cm2, respectively, and at 900 psig, the results were 5.7 and 2.9 µgC/cm^2, respectively. These results suggest that consistently lower deposits can be obtained with the hydrotreated 1:1 RCO/LCO fuel. The sulfur content of the hydrotreated mixture of 3:1 RCO/LCO (as received) is 68.1 ppm, which is about four times the sulfur content of the hydrotreated mixture of 1:1

RCO/LCO (as received). In fact the 1:1 fuel has a sulfur content of only 16 ppm.

One strategy in this work was to evaluate the effect of removing peroxides and hydroperoxides that are expected to be present in the fuels due to the practice of storing fuels in the presence of air. It is believed, although not quantified in this study, that the reduction of peroxides and hydroperoxides present in a fuel would result in a reduced rate of formation of carbonaceous deposits when the fuels were thermally stressed. These peroxy compounds serve to initiate the process of fuel degradation and result in deposit formation. By removing these peroxides, the process of degradation should be retarded.

A common way to remove polar impurities from an organic compound or mixture of compounds is to treat the sample with activated alumina or similar material. In this study, Brockmann, Activity Grade I alumina was used. In general, about 100 grams of alumina was used to treat 1.5 liters of jet fuel.

The results of thermally stressing these alumina-treated samples shows that at 500˚C and 250 psig, the hydrotreated mixture of 3:1 RCO/LCO (alumina treated) produced much lower levels of carbon deposit (3.8µgC/cm^2) than hydrotreated mixture of 3:1 RCO/LCO (as received) (33.7µg/cm^2). This benefit was also achieved at 500 C and 500 psig where ~0 ug/cm2) deposit was observed for the alumina treated sample versus 3.9 µgC/cm^2 for the as received sample.

The sulfur content of the filtered sample of hydrotreated mixture of 3:1 RCO/LCO was measured to be 64 ppm, very slightly lower than the as received sample. This implies, but does not prove, that sulfur removal is not causing the very large decrease in the quantity of deposit formation. It is possible that a specific sulfur-containing component that initiates deposit formation is being removed, but it is more likely that the removal of peroxides and hydroperoxides is contributing to the improved thermal stability performance of alumina-treated fuels

In a similar set of experiments in which the fuels were recycled through the reactor for 5 passes, it was found that at 500˚C and 500 psig, the values for 3:1 and 1:1 blends only changed from 3.9 to 5.9 µgC/cm^2 and from 3.6 to 3.1µgC/cm^2, respectively (Table 2). Mechanistically, this implies that components that affect carbon deposit react rapidly to produce deposit in the first pass and are not stable enough to survive and produce additional deposit in subsequent passes. Thus, if they can be removed the fuel should remain more stable.

It is interesting to compare these results to those from the thermal stressing of JP-8, a completely petroleum-derived fuel. Untreated JP-8 produced 5.3-7.0 µgC/cm^2 of deposit when thermally stressed at 500˚C and 250 psig for 5 hours (Table 3). The result for as-received hydrotreated mixture of 1:1 RCO/LCO is almost as good as JP-8 under these conditions and the coal-derived blended fuel only contains 16 ppm sulfur as opposed to the 714 ppm found in the JP-8.

TPO and FESEM/EDS analysis - Using TPO in conjunction with SEM/EDS analysis, an attempt was made to understand the carbon deposit structural and morphological properties resulting from these experiments. Figures 1a and 1b illustrate oxidation profiles of carbon deposits from petroleum and coal/petroleum blended fuels. For most of the examined fuels, mainly three carbon deposit burn-off temperature ranges exist; the TPO peaks before 300˚C, between 300 and 450˚C, and after 450˚C. The carbon deposits burnt away before 300˚C can be attributed to highly amorphous and homogeneously formed, the deposits between 300 and 450˚C are filamentous-more ordered structures containing metal particles which decrease the burn-off temperature, the deposits giving peaks higher than 450˚C are presumably formed due to strong catalytic effect of Ni and Fe alloying elements of Inconel 718 alloy (7).

Figures 1a and 1b show the TPO profiles of carbon deposits from thermal stressing of RCO/LCO (1/1) and RCO/LCO(3/1), respectively at 500˚C and pressures of 250, 500, and 900 psig for 5h. The different pressure experiments indicate that as pressure increases amount of carbon deposit accumulation reduces significantly for both fuels. The dominant TPO peak appeared at 400˚C for 500 and 900 psig pressure experiments indicating that the pressure effect above 500 psig is mostly on the amount of deposit not on the carbon deposit morphology. At 250 psig, however, TPO peaks at 500 and 600˚C were observed and this result strongly indicates the generation of very reactive radical formation resulting in catalytic carbon deposit formation.

SEM images in Figure 2 clearly show the difference between the RCO/LCO fuels blending ratio effect on carbon deposit formation in the presence of Inconel 718 alloy at 500˚C and 500 psig for 5h. The 3:1 RCO/LCO fuel thermal decomposition produced large amount of carbon deposits almost totally covered the alloy surface. However, RCO/LCO 1:1 fuel thermal stressing resulted in significantly less amount of carbon deposition which is in the particulate form on the alloy surface. Therefore, one can conclude that increase in the RCO ratio facilitates the carbon deposit formation, which might be due to higher sulfur content and RCO hydrocarbon composition.

Conclusions

Carbon deposition from aircraft fuels begins at fuel temperatures on the order of 500˚C, depending upon fuel and metal surface properties. In this work it was found that filtering coal-based jet fuels improves performance in thermal stressing studies by lowering the amount of carbonaceous

deposits. Furthermore, the morphology of the deposit is changed. Although measured sulfur contents of the filtered jet fuels were numerically slightly lower than the unfiltered samples, the sulfur contents were not significantly changed by the filtering process. Sulfur contents of coal-based jet fuels are significantly lower than JP-8 and 1:1 HDT RCO:LCO at 16 ppm sulfur is a good fuel. It is believed, although not quantified in this study, that the reduction in deposits is due to a reduction in peroxides and hydroperoxides present in unfiltered, air exposed jet fuel samples. These peroxy compounds serve to initiate the process of fuel degradation and result in deposit formation. By removing these peroxides, the process of degradation is retarded. We are continuing to investigate the chemistry of these observations.

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Table 1. Total Carbon Deposit Amounts from As Received Coal Derived-Blended Jet Fuels Thermal Decomposition on Inconel 718 at 470˚C (Twall=525˚C) and 34 atm (500 psig) for 5 h with a 4 mL/min Flow Rate.

Fuel Type	P, psig	C Deposit, (µg C/cm^2)
HDT 3:1 RCO/LCO	250	33.7
HDT 3:1 RCO/LCO	500	3.9
HDT 3:1 RCO/LCO	900	5.7
HDT 3:1 RCO/LCO	500	5.9 (5 passes)
HDT 1:1 RCO/LCO	250	9.8
HDT 1:1 RCO/LCO	500	3.6
HDT 1:1 RCO/LCO	900	2.9
HDT 1:1 RCO/LCO	500	3.1 (5 passes)

Table 2. Total Carbon Deposit Amounts from Coal Derived-Blended Jet Fuels After Alumina Treatment Thermal Decomposition on Inconel 718 at 470˚C (Twall=525˚C) and for 5 h with a 4 mL/min Flow Rate.

Fuel Type	P, psig	C Deposit, (µg C/cm^2)
HDT 3:1 RCO/LCO	250	3.8
HDT 3:1 RCO/LCO	500	~ 0

Table 3. Total Carbon Deposit Amounts from Petroleum Derived Jet Fuels After Alumina Treatment Thermal Decomposition on Inconel 718 at 470˚C (Twall=525˚C) and for 5 h with a 4 mL/min Flow Rate.

Fuel Type	P, psig	C Deposit, (µg C/cm^2)
JP-8	250	5.3 – 7.0
JP-8	500	1.0
JP-8	900	0.2

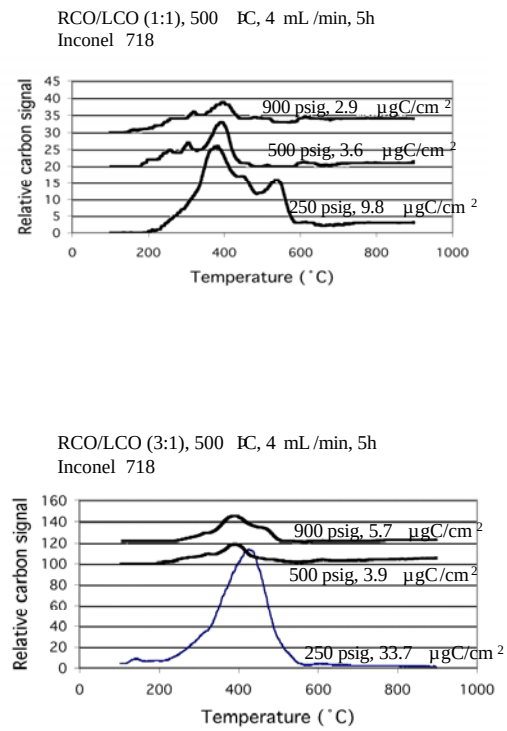
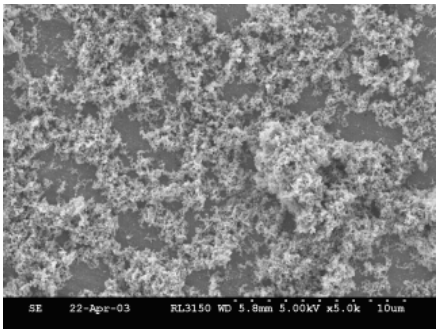


Figure 1. TPO profiles of carbon deposits from thermal stressing of coal-derived-1:1 and 3:1 blended fuels at different pressures on Inconel 718 at 470˚C fuel temperature (Twall=525˚C) for 5h with 4 mL/min flow rate.

RCO/LCO:3/1



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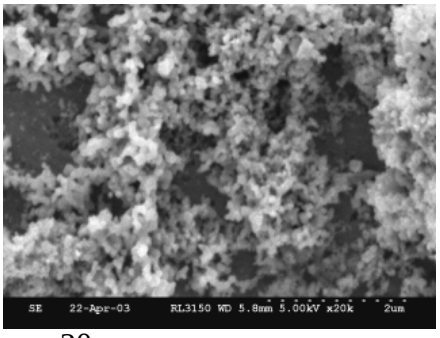
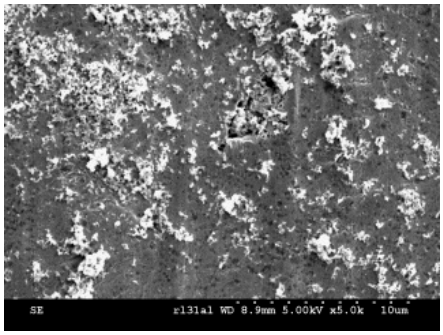


20x

RCO/LCO:1/1



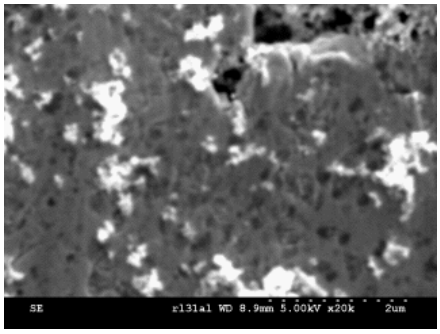


Figure 2. SEM images of carbon deposits from thermal stressing of coal-derived blended fuels on Inconel 718 at 470˚C (Twall=525˚C) and 500 psig for 5h with a 4 mL/min flow rate.