

POTENTIAL STABILIZERS FOR JET FUELS SUBJECTED TO THERMAL STRESS ABOVE 400°C: 2. NMR STUDIES.

Maria Sobkowiak, Leena Selvaraj, Emily Yoon and Michael M. Coleman*
Department of Materials Science and Engineering
The Pennsylvania State University
University Park, PA 16802

Keywords: Jet Fuels, Thermal Stabilizers, NMR

INTRODUCTION

We recently reported^{1,2} the results of Fourier transform infrared (FTIR) and visual studies of Jet A-1 samples that had been subjected to thermal stresses for varying periods of time at a temperature of 425°C. FTIR spectroscopy was shown to be an excellent experimental method that has just about the right degree of sensitivity for our purposes, as it probes at the level of the functional group and is capable of unveiling the major reactions that lead to the formation of carbonaceous solids during thermal stressing at these high temperatures. From these leads we have been successful in identifying a number of additives, specifically benzyl alcohol and 1,4-benzene dimethanol, that appear to function as hydrogen donors and which perform well as thermal stabilizers, significantly retarding the onset of carbonaceous solid formation in jet fuels at temperatures in excess of 400°C.

Evidence obtained from the infrared studies performed to date suggests that the primary route to carbonaceous deposits at temperatures above 400°C may well be the formation of olefins, followed by cyclization and aromatization, similar to the mechanism suggested for the degradation of polyacrylonitrile copolymers used in the formation of carbon fibers³. The focus of our research thus turned to studying molecules that might act as hydrogen donors in the anticipation that they might resaturate the double bonds as they are produced and ultimately retard the subsequent reactions that result in the formation of carbonaceous solids. Hydrogenation agents employed in coal liquefaction, such as tetralin or tetrahydroquinoline, do act as thermal stabilizers and significantly retard the formation of carbonaceous solids.

Surprisingly, however, the best thermal stabilizers we found were methanol derivatives, such as benzyl alcohol and 1,4-benzene dimethanol². From infrared studies of the Jet A-1 fuels containing these two alcohols we know that methanol groups *slowly* transform over a period of hours in the jet fuel to aldehydes. A simple mass balance indicates that this is achieved with the loss of two hydrogen atoms and this suggests that benzyl alcohol and benzene 1,4-dimethanol act as *in situ* hydrogenation agents at high temperatures, similar to coal liquefaction reagents, resaturating olefinic double bonds as they are formed and interfering with the process of aromatization and subsequent formation of carbonaceous solids.

While the infrared studies performed to date have been rewarding, parallel NMR studies, which are the main focus of this preprint, were initiated to assist in the interpretation of the changes observed in the infrared spectra as a function of thermal stressing. NMR studies also provide additional information that is useful for the elucidation of the principal reaction pathways that lead to a retardation of carbonaceous solid formation.

EXPERIMENTAL

Samples for these studies were prepared from an essentially additive free Jet A-1 fuel supplied by the Air Force/WRDC Aero Propulsion Laboratory (No. 90-POSF-2747). Benzyl alcohol and benzene 1,4-dimethanol were purchased from Aldrich Chemical Company and used without further purification.

Thermal stressing was performed on 10 ml samples at 425°C in 15 ml type 316 stainless steel micro reactors² under 100 psi of air. The micro reactor containing the sample was purged

* To whom correspondence should be addressed.

with UHP-grade N₂ five times at 1000 psi to minimize the presence of dissolved oxygen and finally pressurized with 100 psi of air. It was then placed in a preheated sand bath at 425°C for the required reaction time, followed by quenching into cold water and depressurization to remove head space gases.

Samples for NMR analyses were prepared as 15 wt % solutions in deuterated chloroform. The spectra were recorded on a Bruker WP200 instrument at a field strength of 200 MHz.

RESULTS AND DISCUSSION

1. Thermal Stressing of Neat Jet A-1 Fuel at 425°C.

The physical appearance of the neat Jet A-1 fuel after thermal stressing at 425°C under 100 psi of air, changes from a clear, colorless, transparent liquid to a transparent, light yellow liquid after 1h, a slightly turbid, light brown liquid after 3h and a black liquid after 6h. Between 6 and 24h the black liquid becomes progressively more turbid and there is an obvious increasing presence of black carbonaceous solids (color pictures are shown in ref. 2). Changes observed in the infrared spectra of neat Jet A-1 fuel as a function of thermal stressing time led us to consider hydrogen donors as potential stabilizers. Prominent bands at approximately 1642/1652 and 890/910 cm⁻¹ in the spectra were assigned to C=C stretching vibrations resulting from the formation of olefins during thermal stressing. Between 6 and 18h these bands decrease in intensity and are barely detected after 12h in air at 425°C. Other relatively broad bands are observed at approximately 880 and 675 cm⁻¹ and these become increasingly prominent in spectra of the samples after reaction times exceed 6h. These bands were attributed to substituted aromatics and their presence correlates well with the observation of the black carbonaceous material in the thermally stressed fuel at long reaction times.

Figure 1 shows ¹H NMR spectra (0-10 ppm) recorded at room temperature of Jet A-1 fuel samples thermally stressed under air after time periods of 0, 1, 3, 6, 12, 18 and 24h at 425°C. The NMR spectrum of the neat unstressed fuel is representative of a typical complex hydrocarbon mixture⁴ with prominent lines attributed to paraffinic methyl and γ -methyl protons (0.5-1.05 ppm); paraffinic methylene, γ -methylene, β -methyl and β -methylene protons (1.05-2.0 ppm); α -methyl protons (Ar-CH₃*; 2.0-2.6 ppm); α -methylene protons (Ar-CH₂*-R; 2.6-3.4 ppm); α -methylene protons (Ar-CH₂*-Ar; 3.4-4.5 ppm) and aromatic protons (6.0-9.0 ppm). For completeness, olefinic protons, which are not detected at this scale expansion, resonate between 4.5-6.0 ppm. Upon thermal stressing at 425°C the distribution of aliphatic to aromatic moieties changes in favor of the latter. Systematic increases in the intensity of α -methyl, α -methylene and aromatic protons with corresponding decreases in the intensity of paraffinic methyl and methylene groups are observed. Figure 2 shows ¹H NMR spectra of the same samples (figure 1) scale expanded in the olefinic proton region (4.5-6.0 ppm). In the unstressed Jet A-1 fuel olefinic protons are not detected. However, in the spectra obtained after the sample had been thermally stressed for 1 and 3h there is the obvious presence of NMR resonances that may be attributed to internal and external olefins. In common with the infrared results², the concentration of olefins appears to maximize between 3 and 6h. Thus the NMR results obtained on the thermally stressed neat Jet A-1 corroborate the infrared spectroscopic findings.

2. Thermal Stressing of Jet A-1 Fuel Containing 5% Benzyl Alcohol at 425°C.

As we have demonstrated previously² the addition of 5% benzyl alcohol to Jet A-1 fuel results in a significant improvement in the thermal stability at 425°C, as confirmed by the retardation of carbonaceous solids formation by some 3h. Infrared spectroscopic analysis was informative. A band at 1720 cm⁻¹, assigned to the carbonyl stretching vibration of benzaldehyde was observed to increase in intensity to a maximum after approximately 3h of thermal stressing, decrease somewhat at 6h and was essentially absent at 12h of thermal stressing. Concomitant with these observations bands assigned to C=C stretching vibrations are detected at 1h, rise to a maximum at about 6h and are barely detected at 12h of thermal stressing. Significantly, after 12h of thermal stressing bands assigned to substituted aromatics are present and this again correlates

well with the observation of the black carbonaceous material in the thermally stressed fuel. The interpretation of these results was as follows. Benzyl alcohol and similar molecules *slowly* transform over a period of hours in the jet fuel to aldehydes with the loss of two hydrogen atoms. We believe that they act as *in situ* hydrogenation agents at high temperatures, similar to coal liquefaction reagents, resaturating olefinic double bonds as they are formed and interfering with the process of aromatization and subsequent formation of carbonaceous solids.

Figure 3 shows ^1H NMR spectra (0-10 ppm) recorded at room temperature of Jet A-1 fuel samples containing 5% benzyl alcohol and thermally stressed under air after time periods of 0, 10, 60, 180, 360, and 720 min. at 425°C. A comparison of the spectra of the unstressed Jet A-1 fuel with (figure 3) and without (figure 1) the additive, reveals that benzyl alcohol has a convenient characteristic resonance at 4.74 ppm attributable to the hydroxyl proton of the methanol group. Figure 4 shows ^1H NMR spectra of the same samples (figure 3) scale expanded in the olefinic proton region (4.5-6.0 ppm). In the unstressed sample there is no evidence of resonances attributable to olefinic protons and the spectrum is dominated by the intense line associated with the methanol group of benzyl alcohol at 4.74 ppm. It is significant that the intensity of this line at 4.74 ppm decreases as a function of thermal stressing, but is still present in the spectrum recorded after 6h at 425°C. This implies that benzyl alcohol gradually transforms to benzylaldehyde (see infrared results²) in the Jet A-1 fuel over a period in excess of 6h under air at 425°C. At the same time, the olefinic resonances are clearly observed in the sample thermally stressed for 6h which is consistent with the infrared results and lends support for the *in situ* hydrogenation hypothesis.

ACKNOWLEDGMENTS

This project was jointly supported by the US Department of Energy, Pittsburgh Energy Technology Center and the U. S. Air Force WRDC/Aero Propulsion Laboratory, Wright-Patterson AFB. Funding was provided by the US DOE at Sandia National Laboratories under contract DE-AC04-76DP00789. We also wish to thank Mr. W.E.Harrison III of WRDC, Dr. E. Klavetter of SNL, Professor H. H. Schobert, and Dr. C. Song of PSU for their encouragement and many helpful discussions.

REFERENCES

- (1) Selvaraj, L., Sobkowiak, M. and Coleman, M. M., *ACS Division of Petroleum Chemistry Preprints*, **37**(2), 451 (1992).
- (2) Coleman, M.M., Selvaraj, L., Sobkowiak, M. and Yoon, E., *Energy and Fuels*, submitted.
- (3) Sivy, G.T., Gordon, B. and Coleman, M.M., *Carbon*, **21**, 573 (1983).
- (4) Song, C. et al., *Compositional Factors Affecting Thermal Degradation of Jet Fuels Annual Report, Report for period July 1990 to July 1991*, The Pennsylvania State University.

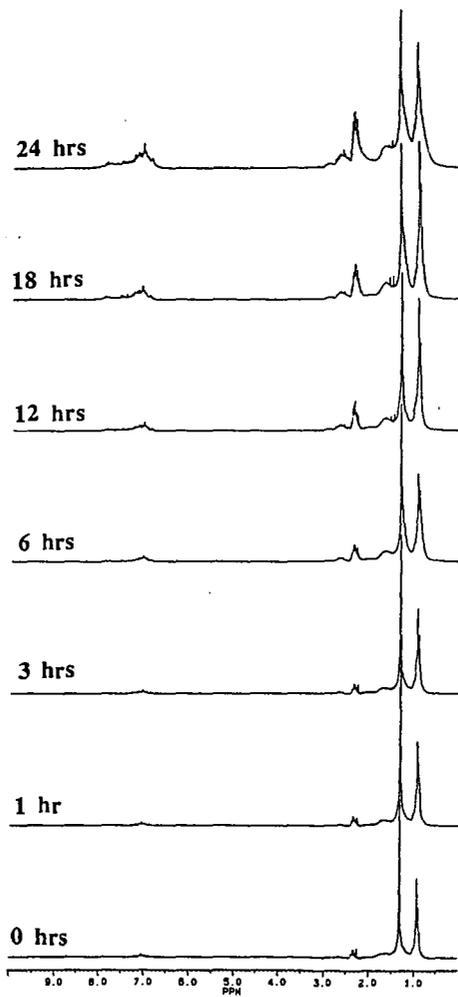


Figure 1. ^1H NMR spectra of neat Jet A-1 fuel thermally stressed for the times indicated over air at 425°C .

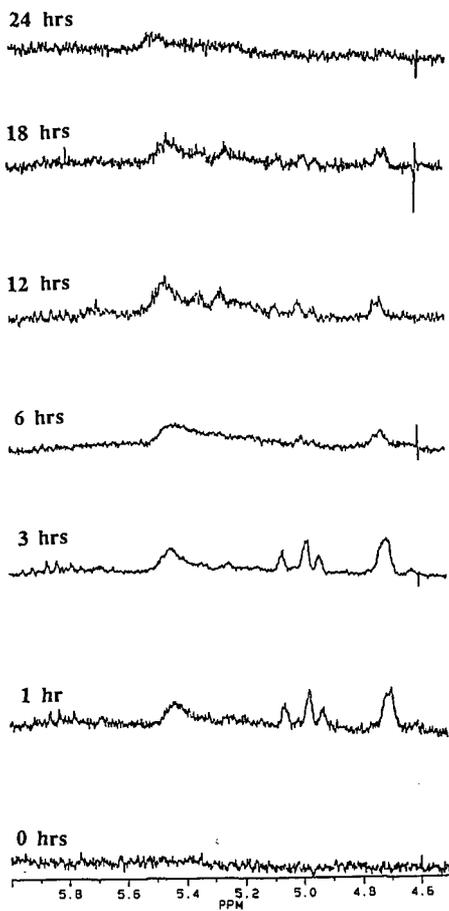


Figure 2. Scale expanded ^1H NMR spectra in the olefinic region of neat Jet A-1 fuel thermally stressed for the times indicated over air at 425°C .

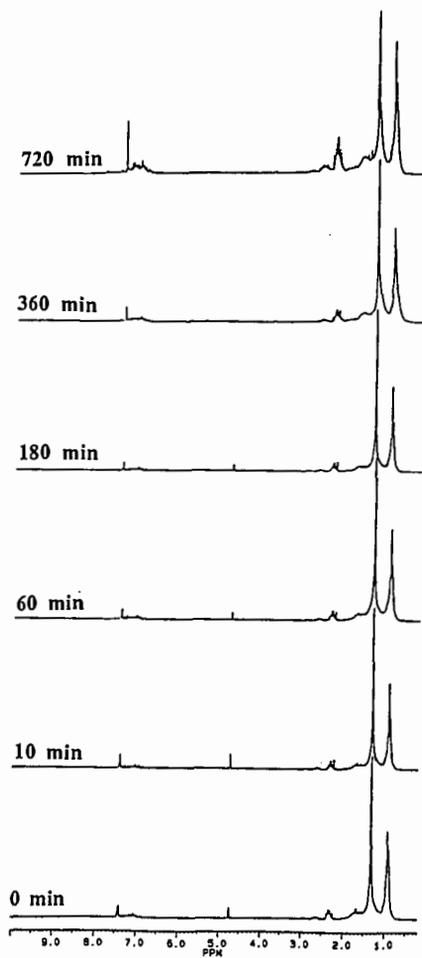


Figure 3. ^1H NMR spectra of Jet A-1 fuel containing 5% benzyl alcohol thermally stressed for the times indicated over air at 425°C .

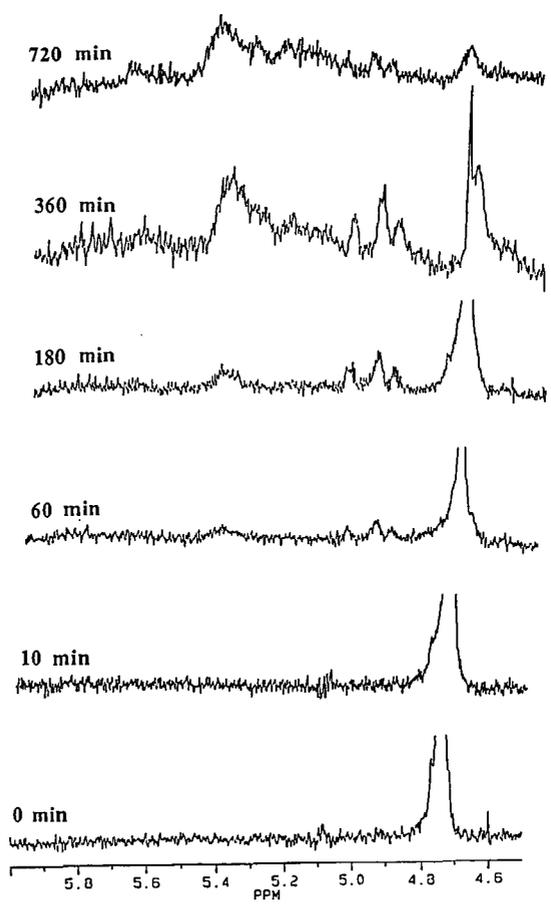


Figure 4. Scale expanded ¹H NMR spectra in the olefinic region of Jet A-1 fuel containing 5% benzyl alcohol thermally stressed for the times indicated over air at 425°C.