Storage Stability Studies of Fuels Derived from Shale and Petroleum

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INTRODUCTION

In considering shale oil as an alternative and complement to petroleum as a feedstock for production of liquid fuels, important compositional differences in the heteroatom components must be taken into account. Some heteroatomic compounds, containing N, S, or O, influence both the thermal stability and storage stability of the liquid fuels. Thermal stability is the resistance of a fuel to formation of deposits on surfaces within the fuel system of an operating vehicle, and storage stability is the resistance of a fuel to formation of gums (both soluble gums and insoluble sediments) under fuel storage conditions. Thermal deposits can foul fuel/lubricating heat exchangers causing decreased efficiency and storage deposits can plug filters.

The purpose of this research is to find mechanisms of storage deposit formation in jet and diesel fuels and to characterize the deposits. Insoluble sediments are the undesirable materials for these fuels since they are injected into engines as liquids. The rate of sediment formation can be determined by traditional quantitative gravimetric procedure, usually at temperatures of 43°C or higher. These procedures require storage times of weeks or months, depending on stress temperature, to develop amounts of sediments which can be measured reliably. However, fuel storage degradation can be monitored in the early stages by laser light scattering of developing particles at ambient temperature. By carrying out extensive light scattering experiments, in the presence of certain heteroatomic compounds, we hope to find out quickly which of these compounds are deleterious to fuel stability. Stability information of this kind is useful in that refining process conditions can then be selected which will minimize fuel degradation through removal of the deleterious compounds. Ultimately, it will be important to know the trade-offs betwen processes of varying severity for removing these compounds and modifying the fuel stability.

EXPERIMENTAL

Laser light scattering measurements were carried out with a photometer described by Berry (1) modified by introduction of a laser light source. Small light-scattering cells of the design by Dandliker and Kraut (2) were used. The Pyrex cells were in the form of truncated cones, in order to reduce the stray light pickup by the detector. In order to study the effects of substituted quinolines, pyridines and indoles on deposit formation, we

adapted the method of Dahlin et al. (3) of obtaining the amount of "deposited gum" from the weight gain of a glass cover slip (22 x 40 mm) placed in a 150-ml Pyrex beaker (bottom surface area 21.61 cm^2) containing 50 ml of liquid fuel.

Degradation products obtained by heat stressing (80-120°C) fuels enriched with specific heteroatomic compounds (500 ppm nitrogen concentration) were analyzed by nuclear magnetic resonance technique. For deposits which are soluble in $CDCl_3$, both 90 MHz and 600-MHz spectrometers were used. The latter instrument operates at magnetic field of 140.9 kgauss, the highest magnetic field possible today, and has been used by Hara et al. (4) to study the very complex coal-derived liquids. For deposits which are insoluble in $CDCl_3$, magic-angle spinning, solid-state carbon-13 NMR spectra were obtained on a Varian XL-200 superconducting spectrometer at 50.3 MHz. Cross polarization of the carbon nuclei was done under Hartman-Hahn matching conditions. The sample was packed into a bullet rotor and spun at approximately 2500 Hz, and sidebands were suppressed using the Dixon Sideband Suppression technique.

RESULTS AND DISCUSSION

(A) Laser Light Scattering and Deposit Formation in Liquid Fuels

Storage techniques for determining the stability of liquid fuels require weeks or months of storage, even at elevated temperatures. A technique which has greater sensitivity for initial deposit formation could shorten the storage time and/or reduce the stress temperature. We have examined one such technique, light-scattering. As a fuel ages, particles grow in size and scatter light. Figure 1 is a plot of scattering intensity at 90° scattering angle as a function of storage time at room temperature for shale II-derived JP-5 (jet fuel, sample J22) containing various concentrations of 2,5-dimethylpyrrole (DMP), while Figure 2 is a corresponding plot for petroleum-derived JP-5 (jet fuel, sample 80-8). The data indicate that in the absence of DMP, which is especially deleterious to fuel stability, the liquid fuel is stable and little light-scattering occurs. As the concentration of DMP increases, the extent of light-scattering increases, in accordance with the increase in tendency to form deposit. The use of light-scattering technique as a monitor of aging has the advantages that room temperature is adequate and that a much shorter time of experimentation is required. The small particles which are formed on aging are believed to be precursors of sediments. Comparison of Figures 1 and 2 shows that the stability of the petroleum-derived JP-5 is less than the shale-derived JP-5.

Figure 3 is a plot of scattering intensity at different angles vs. time at room temperature for petroleum JP-5. For the bottom line, where no DMP is added, the intensity remains small and constant, and independent of the measuring angle. The uper lines are for different angles for petroleum JP-5 with 105 ppm N, DMP. The data show that scattering at 45° is much greater than at 90° or 135°. As the particles get larger, they tend to scatter light more intensely in a forward direction, resulting in a larger value of I_{45}/I_{135}.

Of all the heteroatomic compounds tested, DMP is easily the most powerful promotor of deposit formation in both petroleum- and shale-derived jet fuels. Among some other nitrogen-containing compounds tested, the

deleterious effect on shale jet fuel stability, as measured by the amount of "deposited gum" (3) formed, decreases in the order: 2,6-dimethylquinoline, substituted pyridines (2-ethylpyridine, 2,4,6-trimethylpyridine, 2,6-dimethylpyridine, 2-methylpyridine), 7-methylindole. The following compounds do not form deposited gum in the shale-derived jet fuel even when stressed at 80°C for 8 weeks: 2-methylindole, 2,5-dimethylindole, and 1,2,3,4-tetrahydroquinoline. The DMP sediment is insoluble in the usual organic solvents. The gums obtained from use of other dopants are soluble in $CDCl_3$, and therefore have been studied by solution NMR and infrared techniques.

(B) Liquid State NMR

The JP-5 fuels from shale II and petroleum have essentially identical proton and carbon-13 NMR spectra. The aromaticity is 0.10 and a considerable amount of long unbranched alkyl groups is present in both. Figure 4 gives the 600-MHz PMR spectra of shale-derived JP-5 and 2,6-dimethylquinoline (DMQ), 500 ppm N, 25 days, 80°C: top spectrum, the stressed liquid phase in $CDCl_3$; bottom spectrum, the sediment dissolved in $CDCl_3$. Many NMR signals appear in the lower field regions of the aliphatic and aromatic ranges. These indicate the polycyclic nature of the sediment, 3-4 aromatic rings. Elemental analysis of the gum gives the formula: $C_6H_7O_{1.3}$. The nitrogen content is only 1%. Thus, DMQ (which has 8.9% N) does not dominate the composition of the deposit.

(C) Solid State NMR

Magic angle spinning, carbon-13 spectra of the DMP sediments formed in shale JP-5 and in shale-derived diesel, show that oxygen is incorporated in the deposit in the form of carboxylate, carbonyl and ether linkages. For both fuels, the DMP deposits have the same formula: $C_6H_7NO_{1.5}$. Since DMP is C_6H_9N, we conclude that, unlike DMQ, DMP dominates the composition of the deposits obtained in the shale derived jet and diesel fuels. The nitrogen and oxygen contents of the sediments are 11.6 and 20.1 wt.%, respectively. These values are almost twice the corresponding values of the petroleum jet fuel-DMP sediment which has the formula $C_{17}H_{28}NO_{1.5}$: N,5.1; O,8.4%.

(D) ESCA and Fourier Transform Infrared Spectroscopy

ESCA and FT-IR techniques have been used in the study of deposits formed in shale-derived jet fuel, shale-derived diesel fuel, petroleum jet fuel, and coal liquefaction products which have been subjected to severe hydrotreatment (upgraded H-coal and SRC-II liquids). The results confirm the finding that oxygen is required in formation of deposits and that oxygen is incorporated in more than one species. We are also using these techniques to study the structure of the sulfur and oxygen species of the deposit formed in the jet and diesel fuels, in the presence of DMP and thiophenol, for the purpose of studying synergism.

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REFERENCES

(1) G. C. Berry, J. Chem. Phys., 44, 4550 (1966).

(2) W. B. Dandliker and J. F. Kraut, J. Am. Chem. Soc., 78, 2380 (1956).

(3) K. Dahlin, S. Daniel, and J. Worstell, Fuel 60, 477 (1981).

(4) T. Hara, K. C. Tewari, N. C. Li and F. K. Schweighardt, in "New Approaches in Coal Chemistry" (B. D. Blaustein, B. C. Bockrath, S. Friedman, eds.), ACS Symposium Series, 169, 1981, pp. 289-318.

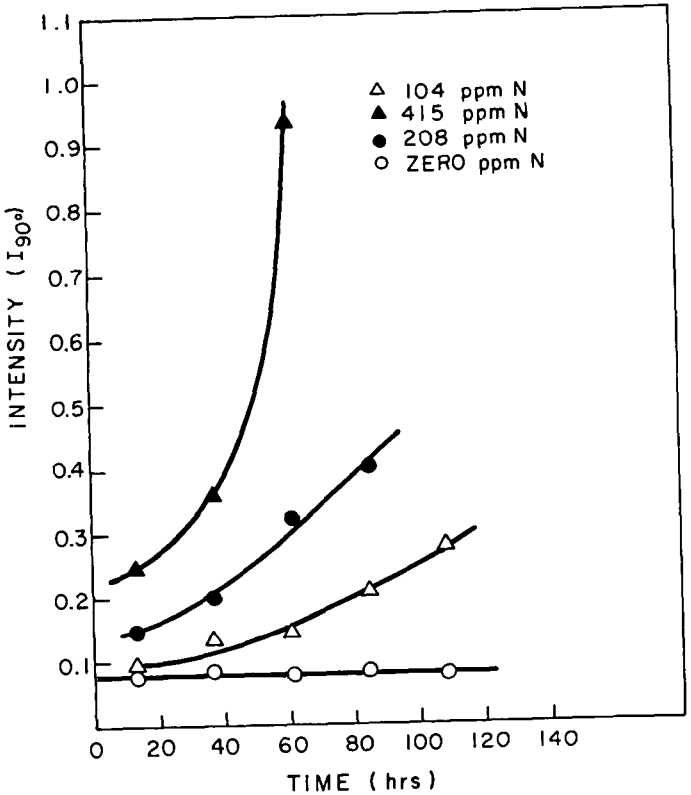

FIGURE 1. SCATTERING INTENSITY, 60°, FOR SHALE II JP-5 + DIFFERENT CONCS. DMP (ppm N) STORED AT ROOM TEMPERATURE.

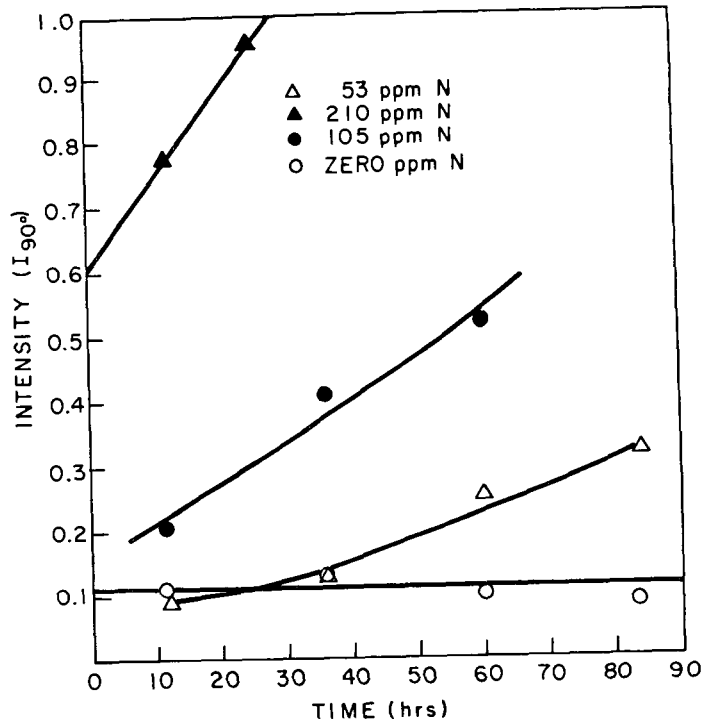

FIGURE 2. SCATTERING INTENSITY, 90°, FOR PETROLEUM JP-5 + DIFFERENT CONCS. DMP (ppm N) STORED AT ROOM TEMPERATURE.

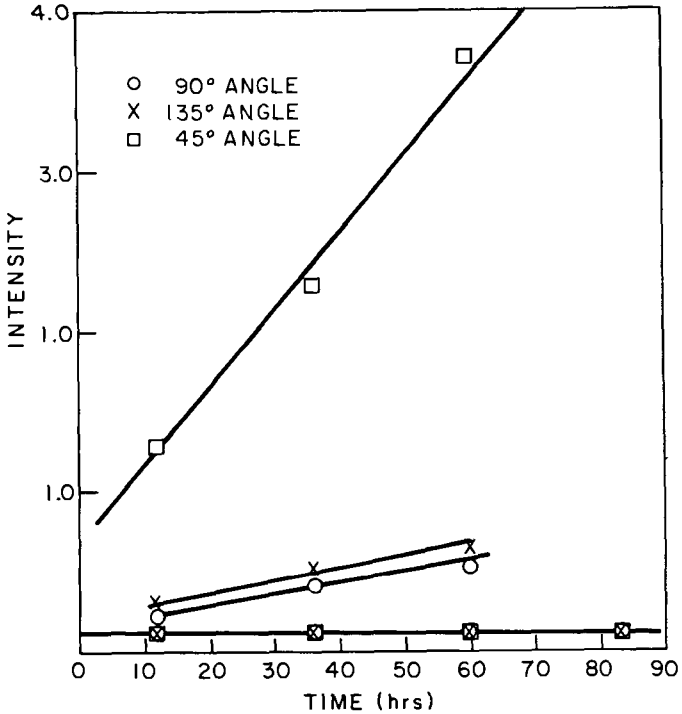

FIGURE 3. SCATTERING INTENSITY AT DIFFERENT ANGLES FOR PETROLEUM JP-5 AT ROOM TEMPERATURE. BOTTOM LINE, NO DMP; UPPER LINES, 105 ppm (N).

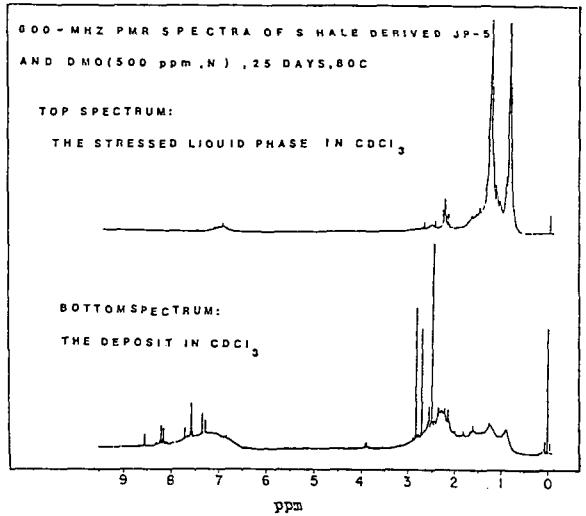

FIGURE 4.