

Oxygen Absorption and Light Scattering Studies of the Stability of Liquid Fuels

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INTRODUCTION

Extensive literature (1, 2) have shown that 2,5-dimethylpyrrole (DMP) is particularly deleterious to stability of liquid fuels, in that this alkylated pyrrole promotes very drastically the formation of insoluble sediments and adherent gums. DMP also promotes extensive light scattering and oxygen absorption, so that their measurements are useful in monitoring the instability of liquid fuels. When the methyl group is on the ring nitrogen in pyrrole, as in N-methyl pyrrole (NMP), the ability to promote sediment formation, light scattering and oxygen absorption becomes much less.

Smith and Jensen (3) have given data on consumption of oxygen by pure pyrroles and have shown that at 323K, the oxygen uptake by DMP is much higher and faster than NMP. The purpose of this research is to determine whether results of oxygen absorption, light scattering and deposit formation can be correlated in studying the instability of liquid fuels. The liquid fuels used are SRC-II and H-coal middle distillates and the upgraded liquids prepared by Chevron Research Co. (4), as well as petroleum-derived JP-5 fuels. Synergistic effects between DMP and thiophenol have been found and are reported in this paper also.

EXPERIMENTAL

The apparatus used for determination of oxygen absorption is shown in Figure 1. It is a semi-closed atmospheric pressure unit in which a static atmosphere of oxygen over an aqueous manometric fluid (Krebs' manometer fluid (5)) is allowed to come in contact with a vigorously stirred sample for ageing. The loss of volatile material during ageing is minimized by the use of an efficient water condenser and a cold trap connected in tandem. In a typical experiment the side-arm flask containing a weighed sample is attached to the bottom of the water condenser. With all the stopcocks open and the reservoir R filled with Krebs' manometer fluid, oxygen gas is passed through the entire system for several seconds. Then the side-arm stopcock is closed and the reservoir is filled with oxygen to a point between the 425 and 450 ml marks. The oxygen inlet stopcock A is then closed and the leveling bulb B is adjusted so as to maintain the same liquid levels in R and B. One or more initial readings of atmospheric pressure, ambient temperature and gas volume in R are made. Additional readings are made, usually 3-5 times a day, for several days, until the liquid level in R neared the "0 ml" mark or the oxygen uptake appeared to stop.

Laser light scattering measurements were carried out with a photometer described by Berry (6) modified by introduction of a laser light source (Spectra-Physics Model 155 0.5 mW He-Ne laser, 632.8 nm). Light scattering cells of the design by Dandliker and Kraut (7) were used. The Pyrex cells were in the form of truncated cones, in order to reduce the stray light pickup by the detector. The additives were weighed in volumetric flasks and then filled to the mark with liquid fuel; the time of mixing was taken as zero time. The liquid was then introduced into a light-scattering cell; the cell was mounted on a cell holder, which in turn was mounted in a cell compartment. Care was taken to insure proper alignment of the cell with the very narrow light beam and the detector. The instrument was calibrated periodically by replacing the cell with a turbid standard glass block. The experiments were conducted at 298 ± 2K.

SRC-II process products were made from Pittsburgh Seam Coal at Pittsburg and Midway Coal Co. These products were blended in the ratio recommended by the Department of Energy Technical officer to represent a typical net whole liquid product from the SRC-II process. The blend is referred to as SRC-II syncrude. H-coal process products derived from Illinois no. 6 coal were blended in the ratio recommended by Hydrocarbon Research Inc. to represent a net whole liquid product from the H-coal process. This blend is referred to as H-coal syncrude. The syncrudes (or middle distillates) were hydrotreated using Chevron's ICR catalyst (containing nickel, tungsten, silica and alumina) at 672 K and approximately 15.6 MPa H₂ partial pressure. The properties of the syncrudes and their upgraded liquids are listed in Table 1 of ref. (4). Petroleum-derived JP-5, no. 80-8 and no. 80-12, were obtained from the Naval Research Laboratory.

RESULTS AND DISCUSSION

Figure 2 shows oxygen uptake curves obtained at 323 K for a middle distillate, an upgraded coal liquid, and petroleum JP-5. The coal-derived middle distillate shows much higher oxygen uptake than the upgraded liquid, which in turn is only slightly greater than the petroleum jet fuel. This means that Chevron Research Inc. have upgraded the coal liquid to about the same stability characteristics (as shown by the extent of oxygen uptake) as the petroleum jet fuel. Other characteristics of the upgraded coal liquids have been discussed in ref. (4).

Figure 3 shows oxygen uptake of SRC-II syncrude at 348 K in the absence and presence of 0.1 g copper shavings per 5 g of fuel. Several investigators (8-10) have discussed copper catalysis of the ageing of SRC-II middle distillate by a *p*-menol oxidative coupling mechanism, and Figure 3 shows that the copper catalysis is also manifested by increase in oxygen uptake.

IR spectra of dilute solutions of SRC-II middle distillate (from Illinois no. 6 coal), before and after ageing for 5 days at 335 K, have been published by Jones and Li (9). The unaged coal liquid exhibits a prominent free hydroxyl stretching band at 3600 cm⁻¹. The intensity of this band is not significantly affected by ageing with copper or oxygen alone; but with both the intensity of this band is reduced. This indicates that the hydroxyl group is modified during ageing, and that the presence of copper is necessary. The unaged coal liquid is completely soluble in pentane. However, after ageing for 5 days with Cu + O₂ at 335 K, 30% of the aged coal liquid became insoluble in pentane. The insoluble fraction contained 3.5% copper in oxidation state II (10). The fact that copper (II) is present signifies that it acts as a reactant in addition to its role as a catalyst.

Iron (II) phthalocyanine (PcFe) also acts as a catalyst in the oxygen uptake by H-coal middle distillate, as shown in Figure 4. In the absence of PcFe, a long induction period of 160 hrs. exists. In the presence of 0.025 g PcFe in 5 g of the middle distillate, the induction period disappears, and a significant oxygen uptake occurs. This constitutes an example of the use of PcFe as a catalyst in the oxidation of coal liquids. Kropf (11) has previously proposed that, in the oxidation of cumene below 373 K, copper phthalocyanine activated a molecular oxygen through its coordination with the metal ion to form a phthalocyanine-O₂ complex, which then abstracted the tertiary hydrogen of cumene to initiate the oxidation. Hara et al. (12) found that the addition of a small amount of pyridine to metal-Pc and cumene mixtures induced a drastic shortening of the induction period and a considerable increase in oxidation rate. In our experiment (Figure 4) addition of pyridine is not necessary, since the H-coal middle distillate already contains many nitrogen-containing compounds.

Figure 5 gives plots of moles O_2 absorbed per mole of N-methyl pyrrole (NMP) vs. time at three temperatures. Increase in temperature means increase in accelerated ageing and therefore results in greater oxygen uptake. At a given temperature, longer storage time results in more ageing and greater oxygen uptake. Jones, Hardy, and Hazlett (13) have shown that for petroleum-derived diesel fuel marine, increase in stress temperature results in a shorter time necessary to form equivalent weights of total insolubles. The data of Fig. 5 also show that increase in temperature results in a shorter time necessary to absorb equivalent amount of oxygen per mole of NMP. A plot of $\log t$ vs. $1/T$ can be constructed, where t is the time in hours required at any particular temperature of stressing to absorb 0.01 mole O_2 /mole NMP. The plot is almost linear. Figure 5 also shows that 2,5-dimethylpyrrole (DMP) exhibits much higher oxygen uptake than does NMP. This is in line with the fact (1, 2) that DMP promotes very drastically the formation of insoluble gums and light scattering in fuels, whereas the effect of NMP is very small. Reactions leading to sediment formation may be characterized as free radical, autoxidative reactions. The greater extent of radical formation in DMP may explain in part the greater oxygen uptake by DMP than NMP and the greater ability to promote deposit formation and light scattering, by DMP than by NMP.

Figure 6 shows plots of light scattering intensity at 90° scattering angle for petroleum JP-5 containing 50 ppm (N) DMP and various additives. The presence of 0.2M thiophene, 0.2 M 1,5-hexadiene, or 0.2M thiophenol alone in the petroleum JP-5 results in no change in I_{90} . In the presence of DMP however, thiophenol gives the largest light scattering followed by hexadiene and then thiophene. The implication is that these individual sulfur-containing compounds by themselves are not deleterious to the stability of the liquid fuel. However, in the presence of nitrogen-containing compound like DMP, the instability effect is shown. Therefore, the combined effect of nitrogen and sulfur-containing compounds must be considered. Figure 7 shows similar plots for upgraded H-coal. Here the scattering angle is 45° , because the intensity at 90° is too small to differentiate between the different additives. The order of instability is: thiophenol > 1, 5-hexadiene > 1-hexene, thiophene.

Figure 8 gives plot of I_{90} vs. time for 2,6-dimethylquinoline (DMQ) and additives vs. time.

In our experiments, positive synergism involving DMP or DMQ is greatest for thiophenol, and the order of other sulfur compounds and unsaturated compound, is the same, whether the fuel is petroleum, upgraded H-coal or upgraded SRC-II liquids. DMQ has less effect on light scattering than DMP, and promotes much less deposit formation than DMP.

CONCLUSIONS

Coal-derived middle distillates have higher oxygen uptake than upgraded coal liquids, which in turn are only slightly higher than the petroleum jet fuel. DMP promotes oxygen absorption, light scattering, and deposit formation, much more than NMP. These three techniques can be correlated in studying the instability of liquid fuels. Synergistic effects between nitrogen and sulfur-containing compounds are apparent.

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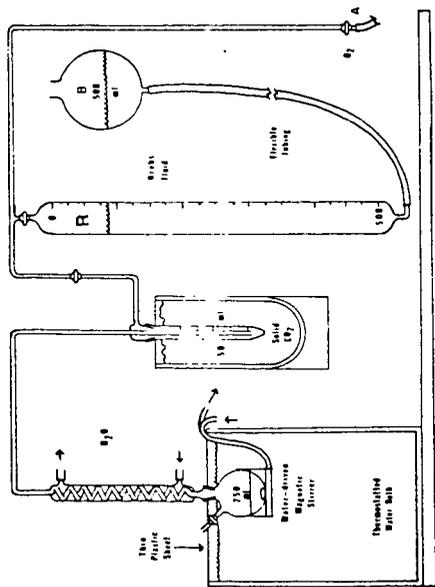
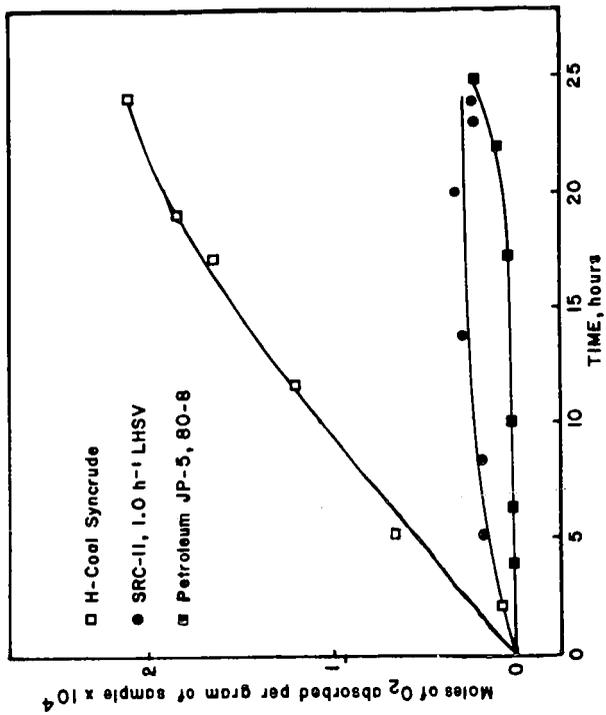


Fig. 1 Apparatus for oxygen-consumption measurement Fig. 2 Oxygen uptake by liquid fuels at 323 K

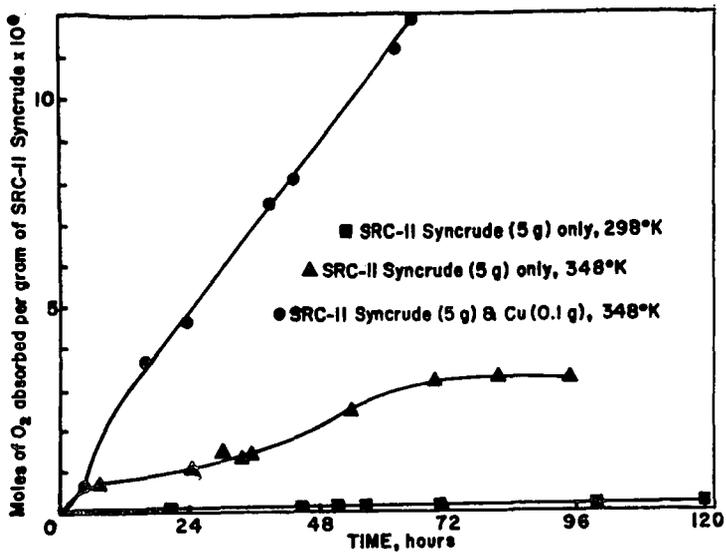


Fig. 3 Oxygen uptake by 5g SRC-II syncrude with and without Cu (0.1g)

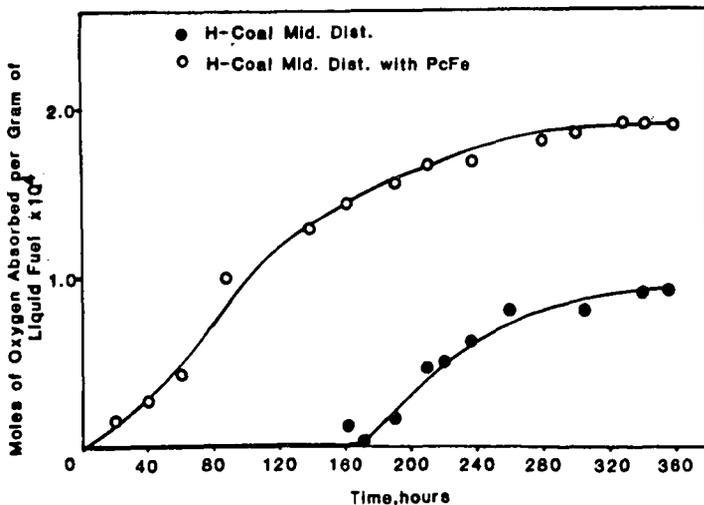


Fig. 4 Oxygen uptake by 5g H-coal middle distillate with and without Pc Fe (0.025g), 296 K

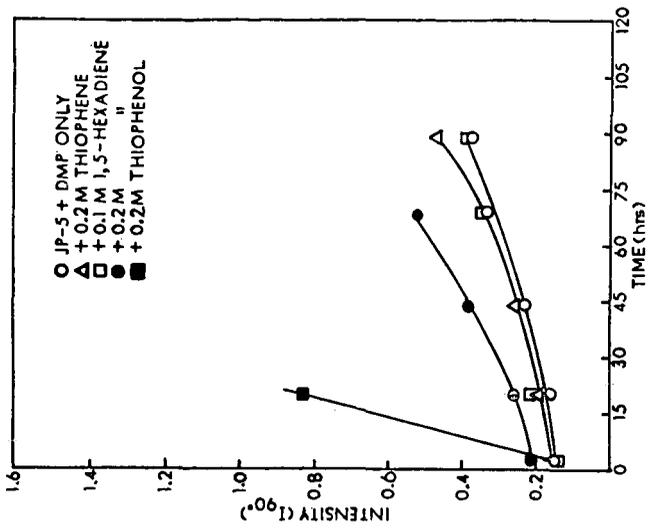


Fig. 6 Light scattering curves for petroleum JP-5, DMP and additives

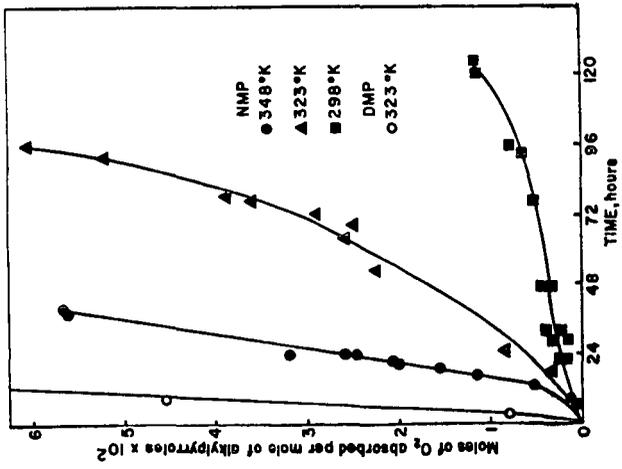


Fig. 5 Oxygen uptake by pure NMP and pure DMP

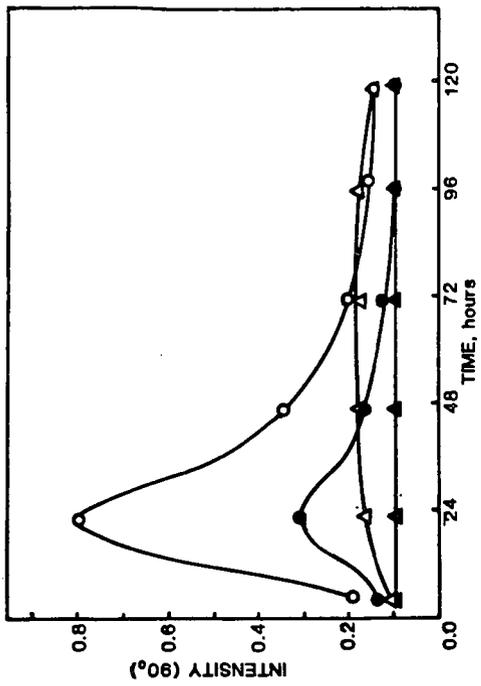


Fig. 8 Light scattering curves for upgraded SRC- II (LHSV 0.5) plus additives:
 ▲ : 0.036M DMQ only; 0.1M thiophenol only
 △ : 3-mercaptopropionic acid (MPA), 0.1M:
 ● : 0.036 M DMQ + 0.1 M MPA
 ○ : 0.036 M DMQ + 0.1 M thiophenol

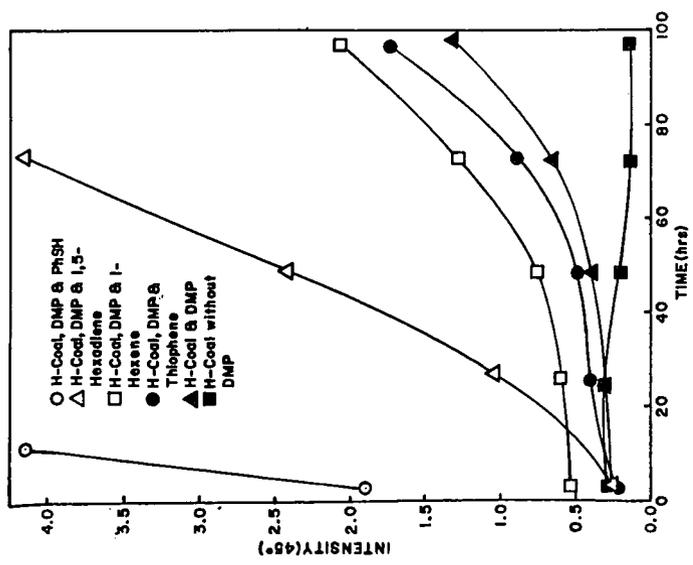


Fig. 7 Light scattering curves for upgraded H-coal (LHSV 0.5) DMP (0.021 M) and additives (each 0.1M)