NASA Contractor Report 168121

OXIDATION AND FORMATION OF DEPOSIT PRECURSORS
IN HYDROCARBON FUELS

Frank R. Mayo, Bosco Lan, David B. Cotts,
S. E. Buttrill, Jr., and G. A. St. John

SRI International
Menlo Park, California 94025

March 1983

CONTENTS

1. SUMMARY

A stable (Fuel A) and an unstable (Fuel C) jet turbine fuel and n-dodecane were distilled under vacuum and oxidized alone and with additives in air at 130°C. The rate of oxygen absorption was measured by gas chromatography of the remaining air; the amount of the gum formation was measured by a new method developed at SRI International. Precipitate formation, if any, was noted. Dodecane oxidizes fastest and gives very little gum. Fuel C oxidizes slower and gives the most gum. Fuel A oxidizes slowest and gives little gum.

Oxidation of Fuel C at low oxygen pressures gave less gum formation and much less oxygen absorption, but it gave much more gum for the amount of oxygen absorbed; however, this result needs confirmation. When polar compounds are removed from Fuel C by chromatographing it over acidic alumina, it oxidizes faster and gives proportionately more gum. The adsorbed polar materials contain 19% (O + S, not distinguished) and a lower H/C ratio (0.98) than the original fuel (1.62). Addition of adsorbed polar concentrate to chromatographed fuel gave poorly reproducible results.

A little indene (0.01 M) retards the oxidation of fast-oxidizing dodecane, but 1 M indene accelerates the oxidation; all proportions give more gum. Both 0.01 and 0.1 M N-methylpyrrole (NMP) greatly retard the oxidation of dodecane but reduce gum formation only moderately. 0.1 M NMP accelerates the oxidation of slow-oxidizing Fuel A and greatly increases gum formation. In general, the additive reacts faster and forms much of the gum. These results are interpreted on the basis of the classic cooxidation of cumene and tetralin.

Unoxidized Fuels A and C were compared by analyses by field ionization mass spectrometry (FIMS), which does not distinguish between paraffins and alkylnaphthalenes, and elemental analyses. The results can be reconciled if unstable Fuel C contains about 20% more alkylnaphthalenes and less paraffins than stable Fuel A. Otherwise, the differences between the compositions of fuels seem minor.

With pure phenylcyclohexane as an example, C_{12} oxidation products can be determined satisfactorily by gas chromatography/mass spectrometry, but FIMS is unsurpassed in quantitatively determining C_{24}, C_{36}, and C_{48} products of various oxygen contents. The new SRI gum method is superior for qualitative comparisons of fuel stability.

1

2. INTRODUCTION

The objective of this research is to determine the mechanism by which gum and deposits are formed in jet turbine fuels and thus how to predict and prevent their formation.

During the year preceding the present contract, we established by field ionization mass spectroscopy (FIMS) that deposit formation from an unstable turbine Fuel C, oxidized at 130°C in air, proceeded by a stepwise condensation process to give products of two or three times the molecular weights of the fresh fuel (plus additional oxygen), and that less soluble products then separated from solution. However, the complexity of the original fuel and the increased complexity of the oxidation products precluded detailed consideration of mechanisms. We therefore investigated the oxidation of pure n-dodecane. Although this material oxidizes considerably faster than Fuel C, it gives little gum and no deposits. FIMS analyses were complicated by fragmentation of the dodecanols and dodecyl hydroperoxides, but enough precursors were found to show that up to four oxygen atoms were present in some C_{24} products and to indicate that C_{12} oxygen compounds are more easily coupled than the dodecane. This work is summarized in a previous annual report.[1]

The present report describes new oxidations and cooxidations of a relatively stable turbine Fuel A as well as Fuel C and dodecane and presents our ideas of the significance of these results. Section 4 summarizes our efforts to follow gum and deposit formation by size exclusion and high pressure liquid chromatography.

3. OXIDATIONS OF FUELS

3.1. Fuel A Alone

The present year's work began with an investigation of Fuel A, a stable jet turbine fuel, received from NASA-Lewis in late 1980. This fuel was distilled at 670 Pa (5 torr), where it boiled at 48°-90°C. It was then oxidized by shaking under air at 130°C. Oxygen absorption was determined by gas chromatography of the remaining air, all as described in the previous annual report.[1] Soluble gum was also determined by the new SRI method[2] in which approximately 5 mL of fuel is evaporated and dried carefully at 200°C and the res'dual gum is weighed on a microbalance.

Rate and gum data for Fuels A and C are summarized in Figure 1, which shows that Fuel A oxidizes much slower than Fuel C. Distilled Fuel A was initially colorless, but gradually turned on oxidation to a clear yellow. Solid deposits appeared only on very long heating. Our results show that our analytical methods are consistent and that oxidation rates are fairly reproducible, at least after the initial stages. Two experiments of different duration (open symbols) were nearly identical. At the end of the slowest run, the hydroperoxide content of the fuel was found to be 1.12 μmole/g fuel, 14.7% yield on the oxygen absorbed. In these experiments, gum formation increases with the amount of oxygen absorbed.

For the first and slowest oxidation of Fuel A, the reaction flask was rinsed only with acetone and water and then baked in a glass-annealing oven. In later runs, the flasks were cleaned by heating with nitric acid, followed by rinsing with distilled water and reagent acetone. We are not sure that the change is significant.

Our previous annual report[1] showed the development of dimers and trimers of unstable Fuel C on oxidation at 130°C. Similar FIMS experiments have now been performed with stable Fuel A, but over much longer oxidations times. Differences in products with m/z components <250 are unimportant, but large differences among the three FIMS spectra appear at m/z >250. Figure 2 shows the buildup during oxidation of dimers and trimers of the original hydrocarbons on two scales, as a proportion of the total peak heights for all compounds measured (including those of m/z <250) and in comparison with a known concentration of perylene standard before evaporation of the 0.1-mL
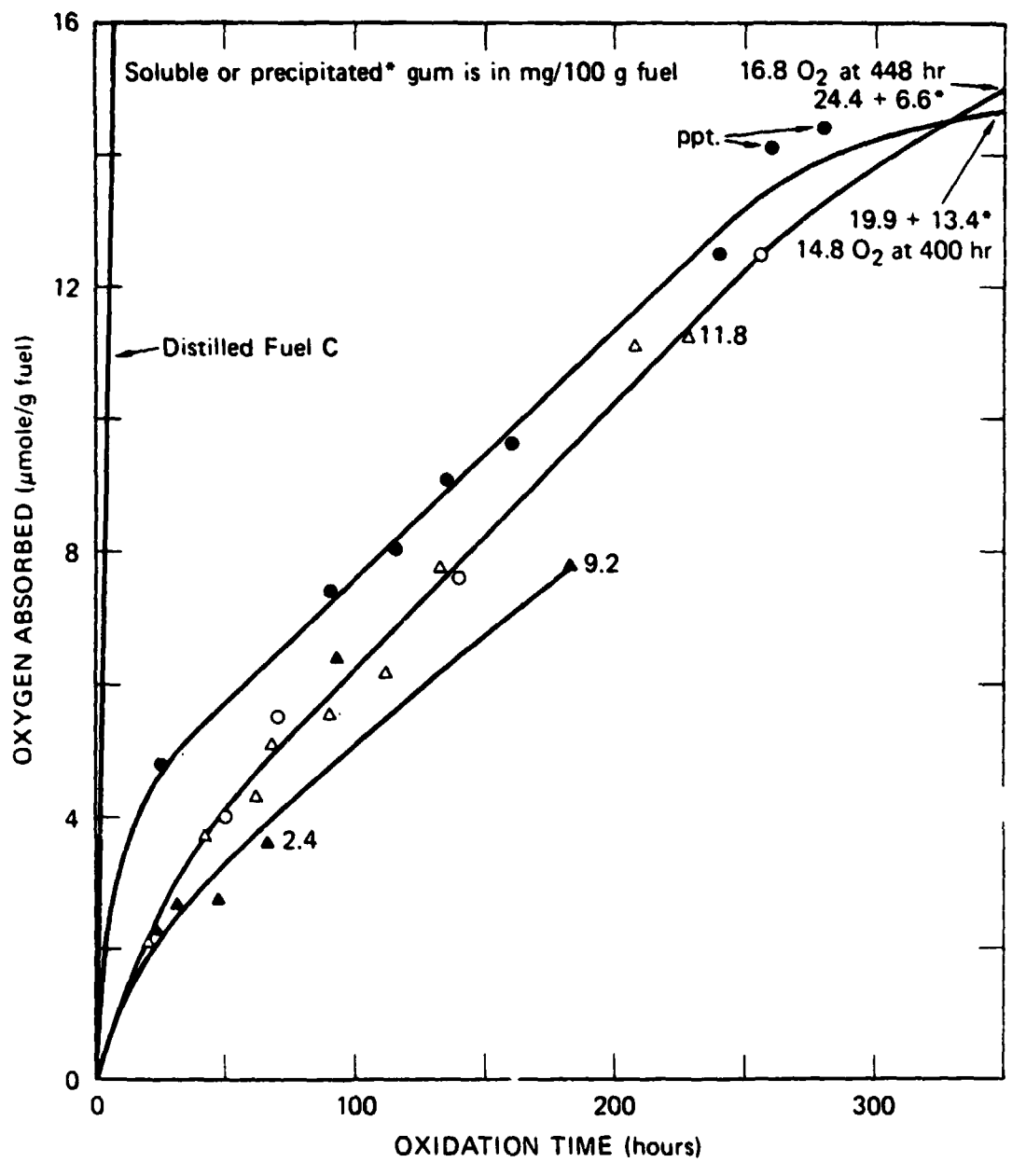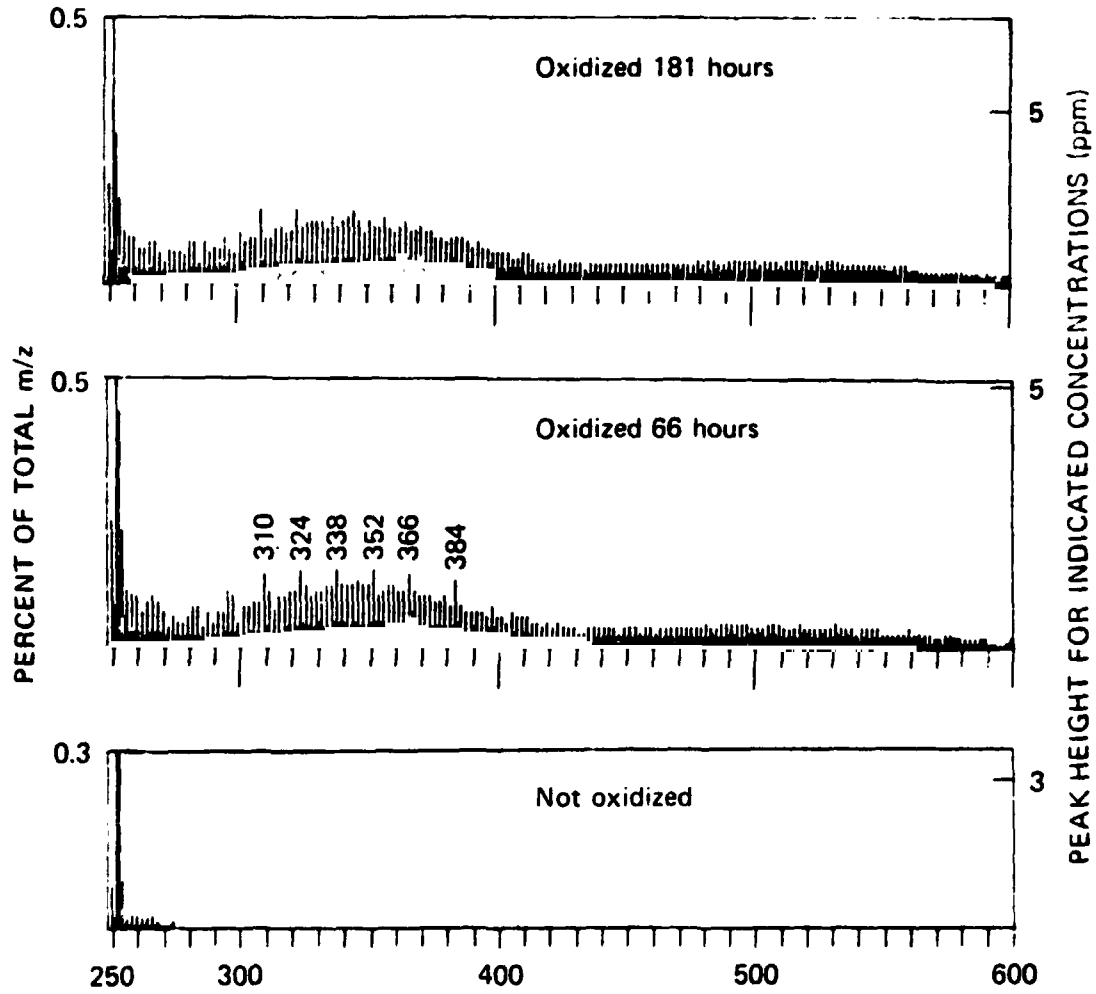
3

FIGURE 1   OXYGEN ABSORPTION AND GUM FORMATION BY FUEL A AT 130°C

4

FIGURE 2   DEVELOPMENT OF PRECURSORS DURING OXIDATION OF FUEL A

The scale on the right is based on the known concentration of perylene.

5

samples. The unoxidized product shows only traces of products at m/z = 250 to 274. The 66- and 181-hour products show new groups of products at 300 to 400 m/z (dimers) and then around 500 (trimers). At 66 hours, the marked peaks at 310 to 356 correspond to a homologous series of paraffin hydrocarbons. We suggest that they correspond to radical couplings, respectively, of two undecane molecules, one undecane and one dodecane, two dodecane (or one undecane + one tridecane), dodecane + tridecane, and two tridecane molecules, all of which are major components of Fuel A, with loss of two H atoms for each coupling and no gain in O. These distinctions are less clear at 181 hours because of coupling of other hydrocarbons and the accumulating oxidation products. Oxidations of Fuel C lasted 4.25, 7.2, and 11.7 hours and gave more dimers and trimers in these much shorter oxidation times. Thus, after 7 and 11 hours, there was considerable dimeric material present in quantities of 10-15 ppm, as gauged by the 20-ppm standard.

3.2. Oxidations of Fuel A with N-Methylpyrrole

The effect of small proportions of NMP (N-methylpyrrole) on oxidations of Fuel A was investigated and then, because of unexpected results, repeated. All these experiments are summarized in Figure 3, where the lowest line corresponds to the top curve in Figure 1. This figure shows that 0.1 M N-methylpyrrole greatly accelerated the oxidation rate of Fuel A at 130°C; led to much earlier separation of deposits (at 17.5 hours instead of 260 hours); and increased the gum formation to 26.4 mg/100 g at 60 hours compared with only 19.9 mg/100 g at 399 hours. The gum formed in the NMP run is considerably less than the NMP added. Peroxides were found in the short NMP run (16.65% of the reacted oxygen), but not in the much longer run with neat Fuel A.

Elemental analyses of Fuel A, NMP gum (not deposits), and NMP alone suggest and that the gum consists mostly of NMP and an aromatic portion of Fuel A:

6
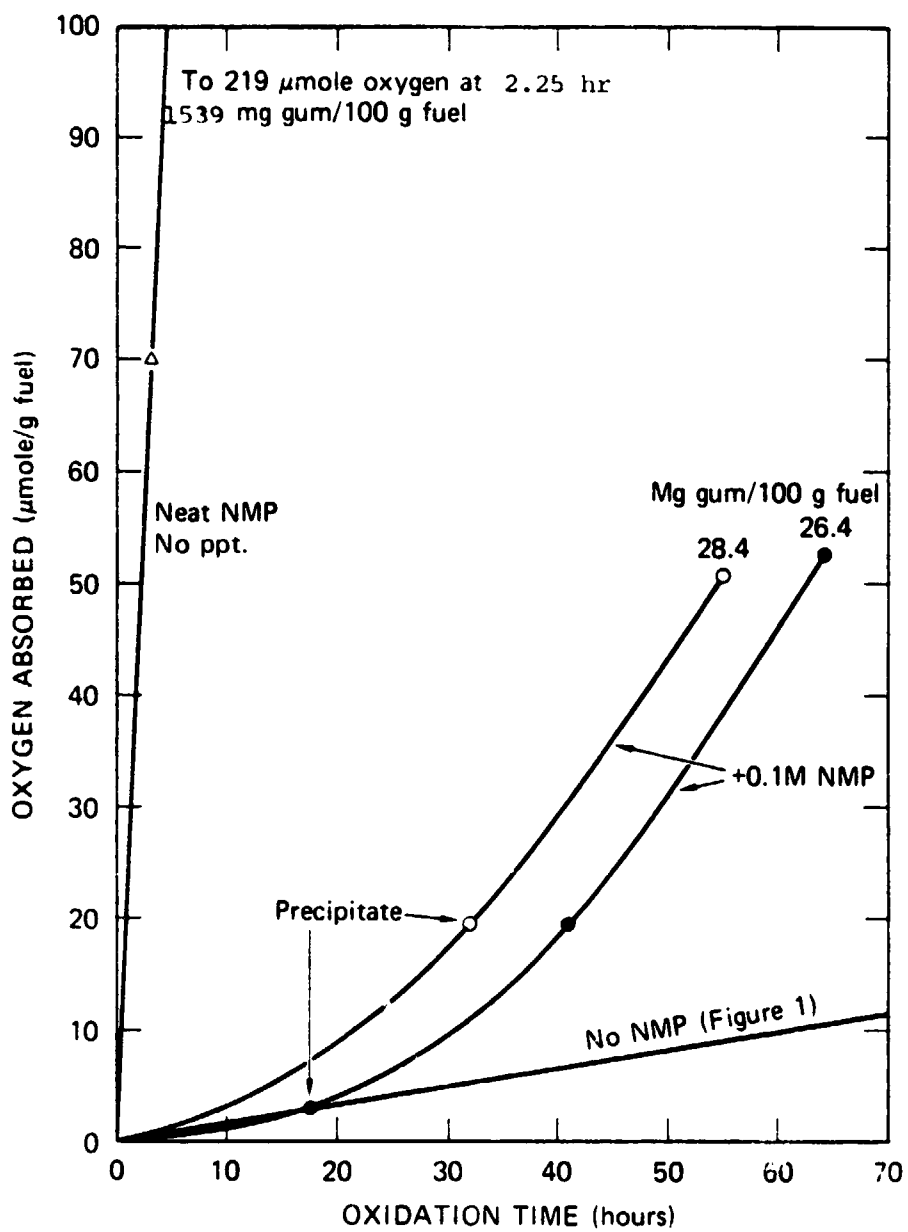
FIGURE 3   OXIDATION OF FUEL A AND NMP AT 130°C

JA-2115-22

	%C	%H	%N	%S	%O diff.	H/C
Fuel A	86.37	13.27	<0.02	<0.02	0.32	1.83
Gum from oxidn. of A + NMP	68.04	5.90	6.17	19.89% O + S (diff)		1.03
NMP, calculated	74.30	7.06	17.27	0		1.40

Figure 3 shows that neat NMP oxidizes very rapidly, about four times as fast at 130°C as neat dodecane, which oxidizes faster than any of the fuels tested. Gum formation from neat NMP was 1539 mg/100 g fuel at 2.25 hours, the highest we have observed so far (Fuel C, 387 at 10 hours).

3.3. Fuel C

Fuel C is the relatively fast oxidizing and unstable No. 2 home heating oil discussed in our previous annual report.[1] Two new and different aspects of its oxidation are discussed here, the effect of oxygen pressure and the effect of chromatography to remove polar materials.

Experiments to investigate the effect of oxygen pressure on the rate of oxidation and condensation of 8.46 g of Fuel C were done at atmospheric pressure with 61.5% O_2 (465 torr) in nitrogen and with 6.35% O_2 (48 torr) at 130°C, with the pressures and proportions of oxygen measured at 20°-25°C. A Servomex Control Ltd. portable oxygen analyser type OA.250 was used to measure the precentage of O_2, and a MKS Baratron type 170M was used to monitor the total pressure.

Figures 4 and 5 show the rates of oxygen absorption in two experiments. In the higher oxygen pressure experiment (Figure 4), there was an induction period of 2.5 hours and then oxygen absorption approached a constant rate of ~12 µmole of O_2/g fuel/hr. The final oxygen pressure at 14 hours was 302 torr when 65% of the initial oxygen had reacted. The low oxygen pressure experiment (Figure 5), however, showed a much lower initial rate of oxygen absorption (0.06 µmole/g fuel/hr) than the higher oxygen experiment (~1 µmole/g fuel/hr) and this low rate decreased steadily, approaching zero when ~42% of the initial O_2 had been consumed, leaving 23 torr in the reactor.
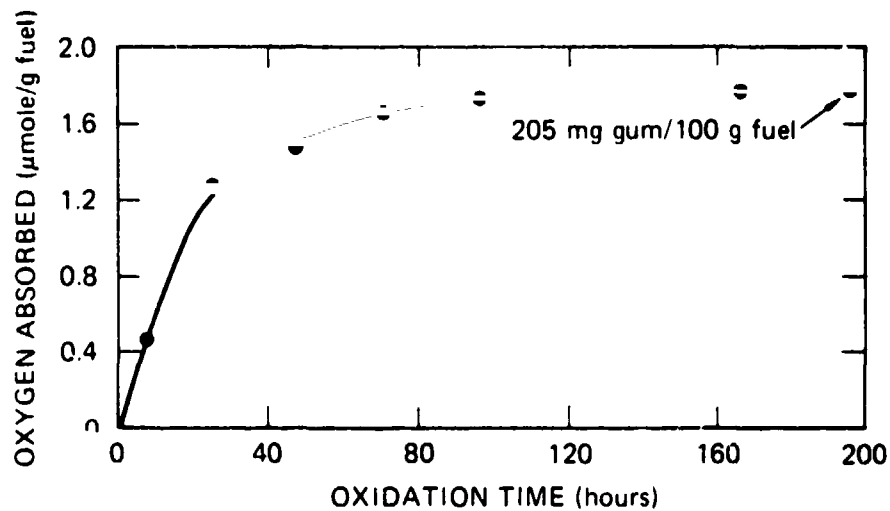
We did not detect any formation of hydroperoxide in either experiment

8
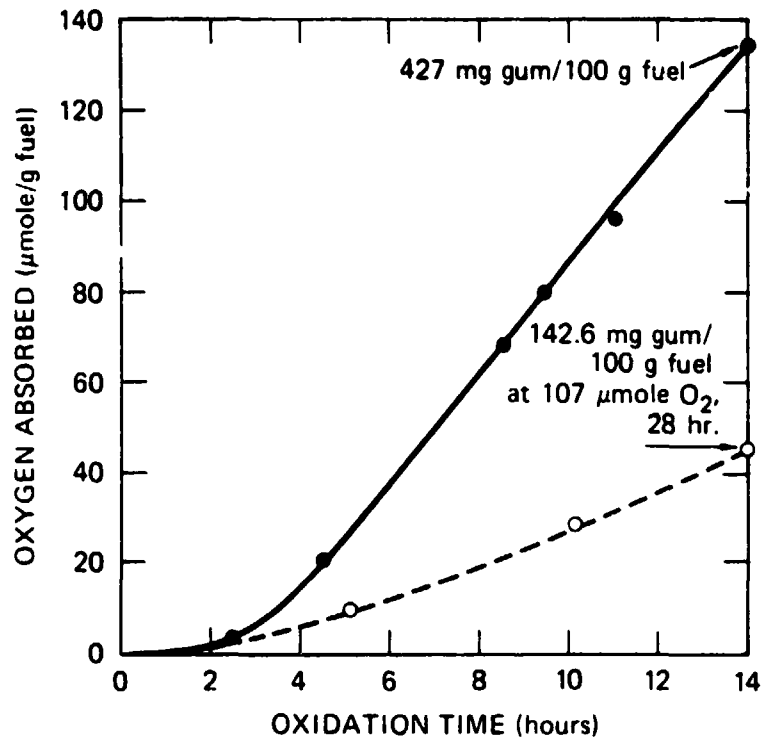
FIGURE 4   OXIDATION OF FUEL C AT 130° AT AN INITIAL OXYGEN
PRESSURE OF 465 torr

Lower curve is for oxidation in air, 150 torr oxygen (Figure 6b) .

FIGURE 5   OXIDATION OF FUEL C AT AN INITIAL OXYGEN PRESSURE
OF 48 torr

9

using our thiosulfate titration method. There was no precipitate formed, only some cloudiness in the higher oxygen pressure experiment, but some solid particles were formed in the low oxygen pressure run. The precipitate in the low O_2 pressure experiment weighed 0.0023 g, 0.027% of starting Fuel C.

Gum formation in mg/100 g fuel is given in each figure. The high pressure run gave only twice as much gum as the low pressure run, although it absorbed 54 times as much oxygen. Thus, much more gum is produced for the oxygen absorbed at low oxygen pressure.

The low pressure oxidation appears to have stopped when only 42% of the original oxygen had reacted. Because of the possibility of a leak in the apparatus or an analytical error, these experiments should be repeated.

Starting with freshly distilled Fuel C, chromatography was used to remove the most polar or active components. A column containing Baker Analyzed "aluminum oxide, acidic" was used. Fuel C was added to the column, and most of it was then eluted with hexane and recovered oy evaporation of the solvent, finally at 4 torr. The alumina was then extracted with nanograde ether, and the polar compounds were recovered by evaporation, finally at 4 torr. The recovered polar portion was 1.42 wt% of the initial Fuel C. Elemental analyses show that this portion of Fuel C is richer in N, S, O, and aromatic material than the average of Fuel C:

	%C	%H	%N	%S	%O diff.	H/C
Fuel C	87.57	11.94	<0.02	0.03	0.17	1.62
Polar concentrate	74.92	5.99	0.20	18.89	O + S (diff)	0.98

Two separate chromatography experiments with Fuel C are summarized in Figure 6. In each experiment, oxygen absorption and gum formation were determined on the original distilled Fuel C, on the chromatographed Fuel C (usually after distillation also), and on reconstituted Fuel C, made by mixing chromatographed Fuel C with an appropriate proportion of recovered polar material. The first set of experiments is summarized in Figure 6a. The low gum formation in the original fuel was unexpected, so this experiment was repeated (lowest curve in Figure 6a); the rate of gum formation was even lower

10
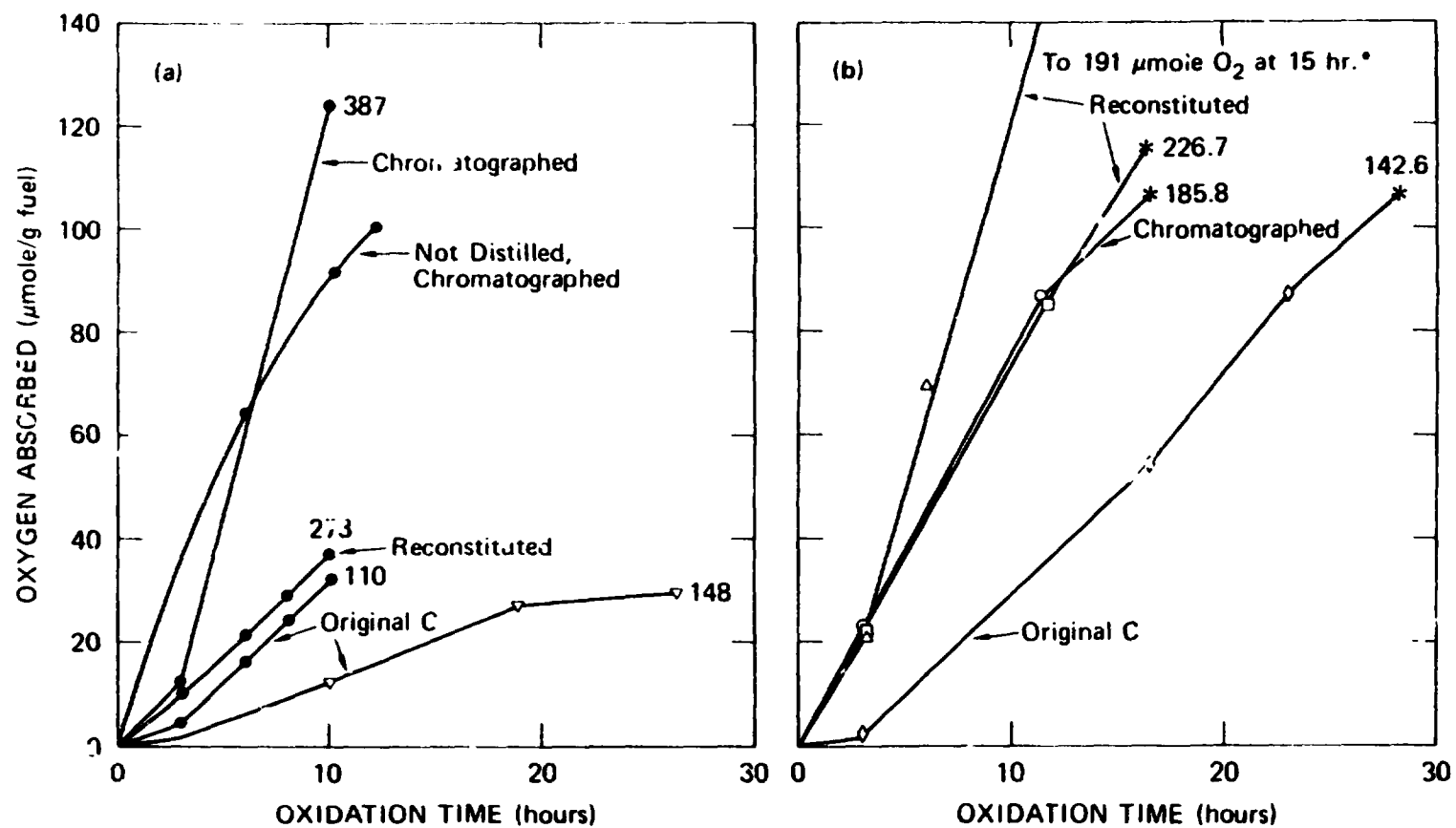
FIGURE 6   DUPLICATE OXYGEN ABSORPTIONS AND GUM FORMATIONS BY FUEL C IN AIR AT 130°C

*Indicates that precipitate was noted.   All fuels were distilled, except as noted   Gum formation is in mg/100 g fuel

11

JA-2115-25

but so also was the rate of oxidation. The chromatographed Fuel C certainly oxidized faster than the original material but whether distillation after chromatography is important is less certain.

Because the five parts of the first set of experiments were conducted over a period of two months and because the original fuel gave the least gum, we conducted a second set of experiments that was finished within two weeks (Figure 6b). In these experiments, oxidations with air at 130°C were conducted with the distilled but otherwise untreated, chromatographed and distilled, and reconstituted Fuel C. Of 33.48 g of Fuel C used for chromatrography, 28.72 g was recovered and distilled and 0.1738 g of extract was obtained after evaporation of the ether extract. To reconstitute Fuel C, we used 0.0572 g of polar extract and 8.35 g of chromatographed and distilled Fuel C for the slower run in Figure 6a, 0.0534 g extract and 8.30 g of the same Fuel C in the faster run in Figure 6b.

Figure 6b shows the oxidation and soluble gum results for each experiment. These results, all obtained within 15 days, are significantly different from those reported for the first set of experiments, conducted over two months, and the gum results are more reasonable. Figure 6b indicates that distilled Fuel C contains retarders that have a marked initial effect on oxygen absorption and a small subsequent effect. Chromatography apparently removes these retarders. The reconstituted Fuel C now oxidizes at the same rate as chromatographed C; the small difference in final rate is of dubious significance. However, a duplicate oxidation of reconstituted Fuel C gave the same initial rate but was 77% faster by the end of 15 hours.

Thus, reproducibility is unsatisfactory in each set of experiments, and between sets. Possibly, changes in fuels occur in storage, even at -12°C under nitrogen. Another possibility is that every distillation of Fuel C results in elimination of the highest boiling 5% of the fuel and that the number of distillations should be minimized. Still another possibility is that oxidations without added initiator will always be poorly reproducible The results in Figure 6 also suggest some parallel between rate of oxidation and rate of gum formation within each set of experiments with Fuel C, although there seems to be no correlation among different fuels.[3]

12

## 3.4. Oxidation of n-Dodecane Containing Indene or NMP

Five oxidations of n-dodecane were conducted at 130°C to determine the effects of 0 to 1 M indene on rates of oxidation and gum formation. We discuss the rates of oxidation first.

With no initiator at 1 atm of oxygen and 50°C, neat indene oxidizes at the rate of 0.034 M/hr, equivalent in our units to 35 μmoles/g/hr. The steady rate for neat dodecane at 130°C is 47 μmoles/g/hr. From the review of Howard,[4] the propagation and termination constants can be compared at 30°C:

$$\text{Dodecane, } k_p = 0.0065 \text{ M/s; } 2k_t = 3 \times 10^6 \text{ M/s; } k_p/(2k_t)^{1/2} = 3.75 \times 10^{-6} \text{ (M/s)}^{1/2}$$

$$\text{Indene, } k_p = 142 \text{ M/s; } 2k_t = 50 \times 10^6 \text{ M/s; } k_p/(2k_t)^{1} = 2.01 \times 10^{-2} \text{ (M/s)}^{1/2}$$

Thus, for the same rate of initiation at 30°C, indene would oxidize 5350 times as fast as dodecane but the difference would narrow at 130°C. Figure 7 shows that small proportions of indene initially retard the oxidation of dodecane and that larger proportions cause oxygen to be absorbed more rapidly.

We now consider the products of oxidation of indene. An alternating 1:1 polyperoxide is formed in high yield.[5] The high molecular portion is only sparingly soluble in hydrocarbons. By analogy with poly(styrene peroxide),[6] poly(indene peroxide) probably decomposes thermally to give a dialdehyde,
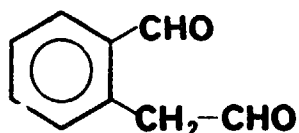
and may not survive our usual gum test. In our cooxidations of dodecane and indene, some light-colored oily reaction products separated during the oxidation and were later collected by centrifuging, but no solid precipitates were observed. To include a maximum of poly(indene peroxide) in the gum, we vacuum-distilled the reaction mixture almost to dryness below 100°C. Gum was then determined as usual[2] except that the drying temperature was held to 100°C for 17 hours. All indene experiments gave more gum than the blank on dodecane, even though more oxygen was absorbed in the blank experiment. Gum formation increases rapidly with the concentration of indene up to 0.1 M indene, where gum formation was >50 times that in the blank.

13

Some gum determinations were made at 200°C instead of at 100°C; these results are also shown in Figure 7. The data suggest that the 200°C procedure finds only about half as much gum as the 100°C procedure for low amounts of gum, but that the difference decreases as the gum increases.

Figure 7 shows that NMP also retards the oxidation of dodecane.[7] This combination will be discussed at two points in the next section.

3.5. Discussion

This section will first compare Fuels A and C. Oxidations of Fuel C were discussed in the previous annual report,[1] and a few of these data have been inserted in Figure 1, which deals with Fuel A. Fuel C oxidizes much faster than Fuel A at 130°C and it discolors more during oxidation. A precipitate appeared between 7 and 11 hours; about 400 hours were required for deposit formation with Fuel A. Molecular weight profiles have been determined by S.E. Buttrill, Jr., and G.A. St. John, using a batch inlet FIMS, and found to be quite different:

Hydrocarbon Class	Alkanes + Alkyl- naphthalenes	Ring or C=C 1 2 3			Alkyl- benzenes	Indanes or Tetralins	M_n
Fuel A, mole %	20.0	16.9	15.7	5.0	28.3	14.1	151
Fuel C, mole %	45.4	10.3	6.9	2.9	19.3	15.2	159

This classification understates somewhat the proportions of saturated hydrocarbons, which are ionized with less efficiency by FIMS, and does not distinguish alkylnaphthalenes from alkanes. A new high-resolution FIMS, expected to be available soon, should eliminate the latter problem.

Elemental analyses are as follows:

	%C	%H	%N	%S	%O (diff)	H/C
Fuel A	86.4	13.3	<0.02	<0.02	<0.3$_6$	1.833
Fuel C	87.6	11.9	<0.02	0.03	<0.1$_9$	1.625

For the FIMS analyses of Fuels A and C to be consistent with the elemental analyses and H/C ratios, Fuel C must contain much more alkylnaphthalenes than Fuel A; it must also contain more sulfur.

14
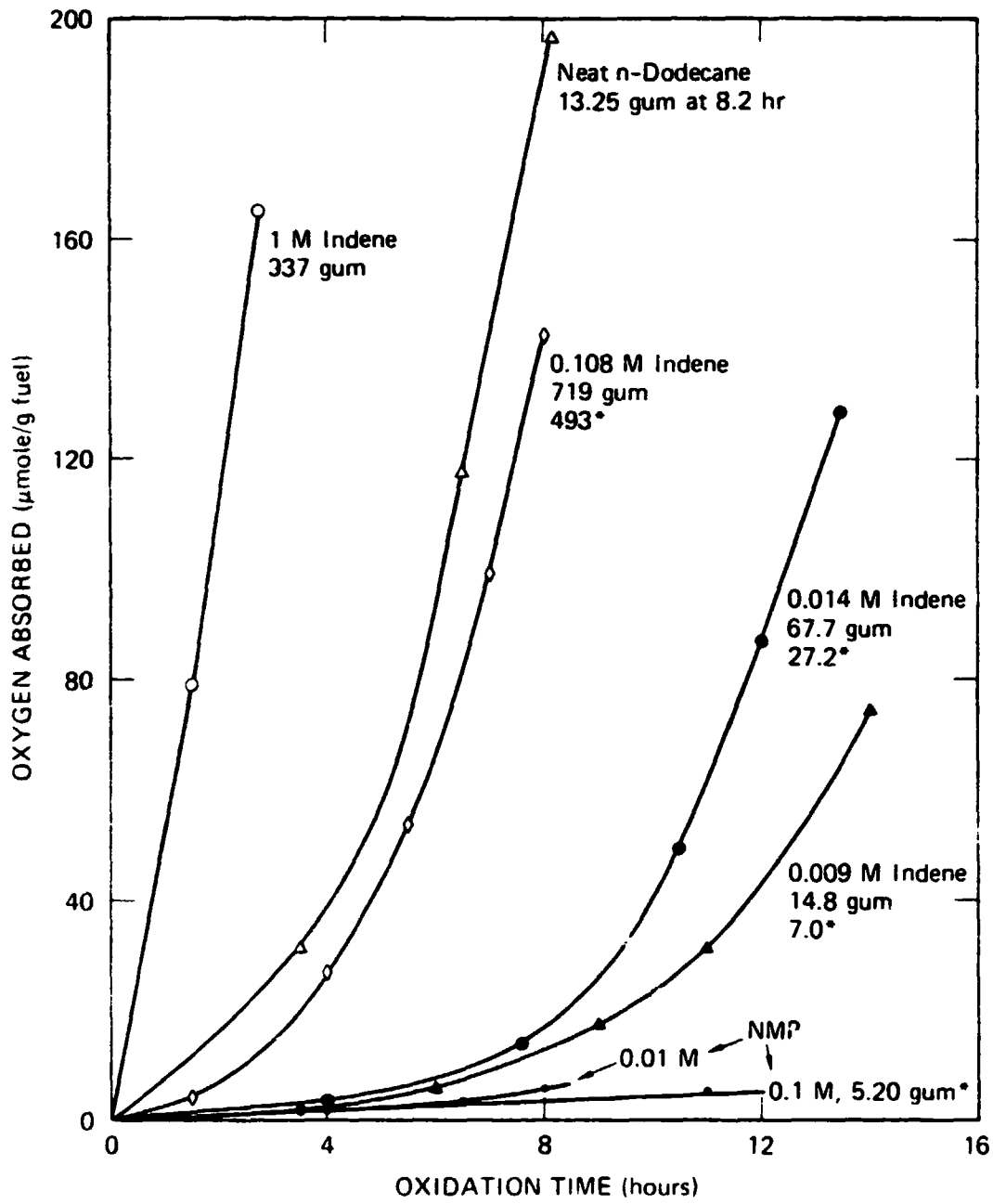
FIGURE 7   OXIDATIONS OF n-DODECANE WITH INDENE AND NMP AT 130°C

Gum is in mg/100 g fuel, determined at 100°C except when marked * for 200°C.

JA-2115-16A

15

In considering the effects of NMP and indene on oxidations of dodecane and Fuel A and the rate effects in cooxidations of hydrocarbons in general, we shall start with the classic cooxidation of cumene and tetralin. Figure 8 summarizes the data of Russell[8] on the cooxidation of cumene and tetralin in the presence of 0.02 M t-butyl perbenzoate (to give constant rate of initiation) at 90°C. The minimum rate appears at 2.8% of tetralin only because additional data are lacking. The important feature of these data is that small proportions of tetralin retard the oxidation of cumene, even though tetralin alone oxidizes faster than cumene alone. The general equation for rate of oxidation of a pure hydrocarbon, RH, is

$$-d[RH]/dt = (R_i/2k_t)^{1/2} k_p [RH]$$

Absolute rate constants at 30°C[4] (because they are available there but not at 90°C) will be used to explain these relations. Tetralin has a propagation constant (k_p) 35 times that of cumene, a termination constant 507 times that of cumene (ratio of $k_t^{1/2}$ is 22.5), and a rate of oxidation (at the same rate of initiation and concentration of hydrocarbon) 1.5 times that of cumene. Thus, a small proportion of tetralin in cumene is relatively rapidly converted to tetralin peroxy radicals, which terminate quickly when they cannot propagate readily with tetralin. A minimum in rate of cooxidation requires that one component have a high propagation constant and the other have a low termination constant, which is characteristic of tertiary alkylperoxy radicals. Plots of rates of cooxidations of most hydrocarbon mixtures are linear or slightly curving functions between the rates of oxidation of the pure hydrocarbons.

We shall use these relations first to account qualitatively for our results on the oxidations of dodecane with small proportions of indene. Indene alone oxidizes faster than dodecane, and apparently has higher propagation and termination constants than dodecane. In cooxidations with 0.006 and 0.014 M indene, the rate increases with increasing concentrations of indene and acts increasingly like oxidations of indene in an inert solvent. Our findings that NMP accelerates the oxidation of Fuel A (Section 3.1) but retards the oxidation of dodecane (Section 3.4[7]) are now considered. Without NMP, n-dodecane oxidizes initially about 40 times as fast as Fuel A (but soon accelerates); with 0.1 M NMP, dodecane oxidizes only about 4 times as fast as

16
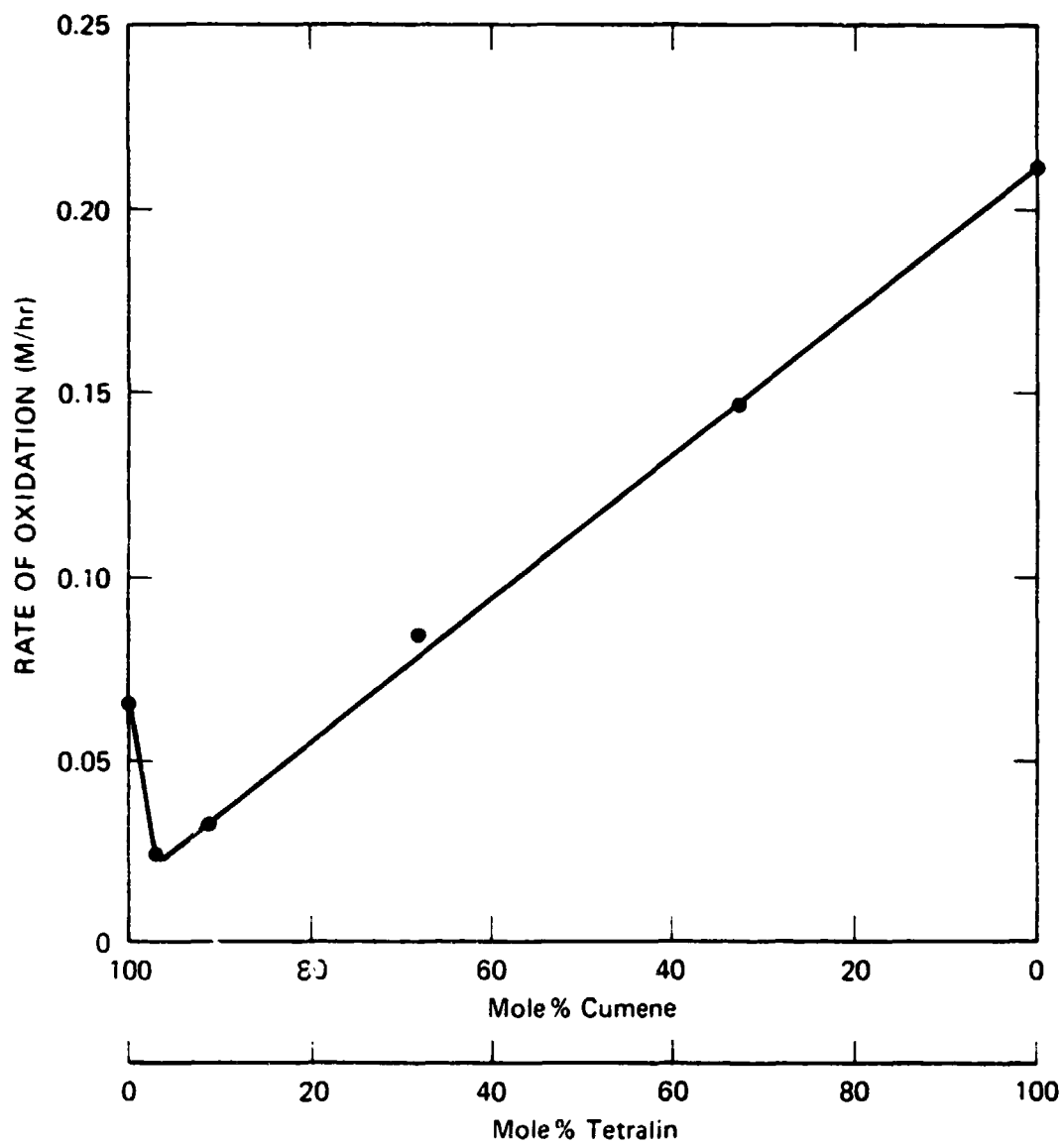
FIGURE 8   COOXIDATION OF CUMENE AND TETRALIN WITH 0.02 M t-BuO$_2$Bz AT 90°C
Data of G. A. Russell (ref. 8)

17

Fuel A. Figure 9 puts these results in perspective. In terms of the cumene-tetralin plot in Figure 8, NMP produces a clear rate minimum with dodecane, but the oxidation of Fuel A is so slow that addition of NMP produces no obvious minimum. If the rate constant for chain termination in Fuel A is close enough to that in NMP, there should be no minimum. The components of Fuel A that are responsible for its low rate of oxidation should be of great theoretical and practical importance. The stability of Fuel A might be due to a stabilizer that survived vacuum distillation, but the longest oxidations of Fuel A in Figure 1 give no indication of exhaustion of any stabilizer. We shall look for small amounts of oxygen compounds that might be stabilizers in our next FIMS analysis.
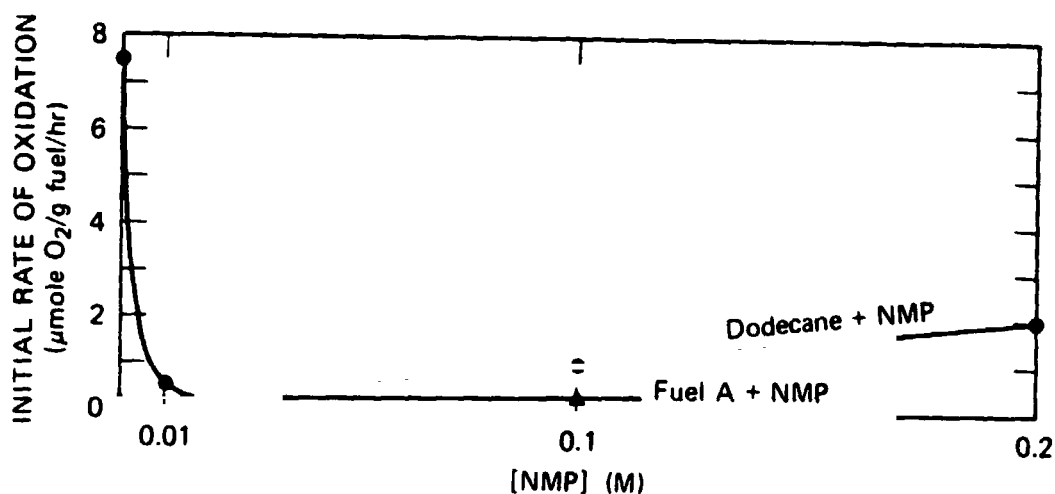

JA-2115-27

FIGURE 9   INITIAL RATES OF OXIDATION OF FUEL A AND n-DODECANE
            WITH NMP AT 130°C

18

In the systems discussed above, the effects of indene and NMP on oxygen absorption and gum formation are associated with the high activities of these compounds in oxidation and their rapid consumption. The effects should disappear as the additives are exhausted. So far, we have no indication that any metal-free organic compound acts catalytically, without being consumed.

This interpretation above appears to explain qualitatively our data on rates of oxidation of fuels in general; all that we have examined oxidize slower than dodecane, even though they are composed mostly of paraffins. We propose that the retardation comes mostly from the small proportions of alkylaromatics that they contain, which apparently have higher propagation and termination constants and would oxidize faster in pure condition than dodecane. However, our interpretations can be no better than qualitative, because we have no measure of, or control of, rate of initiation in our thermal oxidations at 130°C.

A possible complication in these rate and product relations has recently come to our attention. In the cooxidation of n-dodecane and ethylbenzene at 130°C,[9] the rate and product predictions of the cooxidation equation have been found to diverge from experiment; reconciliation requires inclusion of steps such as[10]

$$\text{Decyl} \cdot + \text{PhEt} \longrightarrow \text{decane} + \text{Ph-}\overset{\bullet}{\text{C}}\text{H-Me}$$
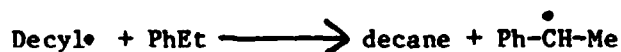
which are fast enough to compete with the reaction of decyl radicals with oxygen. The result is that less decane and more ethylbenzene oxidize than are predicted from the rate equation.[5] This reaction of alkyl radicals is of course favored by low oxygen pressure. The rates in these experiments were complicated further because rates of initiation were unknown in both ours and the Russian work and by the finding[9] that decyl hydroperoxide decomposes and initiates faster than phenethyl hydroperoxide. The importance of hydrogen transfer among various benzyl radicals is unsettled, but it is probably less important than in the conversion of alkyl to benzyl.

4. CHROMATOGRAPHY AND LIGHT SCATTERING AS ANALYTICAL METHODS

4.1. Introduction and Summary

The objective of the research described in this section was to find an economical substitute for FIMS for determining gum and deposit precursors. We chose phenylcyclohexane (PCH) for these experiments because it oxidizes easily and gives useful proportions of deposit precursors.[11] For this C_{12} hydrocarbon, we wanted a method to determine the proportions of C_{12} oxidation products and then, without regard to their oxygen contents, the proportions of C_{24} and C_{36} condensation products.

Size exclusion chromatography, often called gel permeation chromatography, was not useful because our products differed in both oxygen contents and molecular weights. Further, suitable molecular weight standards were not available.

Low angle light scattering for molecular weight determinations requires chemically homogeneous systems. When we found that our oxidation and precursors varied considerably in both oxygen contents and molecular weights and that molecular weights of interest would be low, this method was deemed unsuitable for a serious trial.

High pressure liquid chromatography (HPLC) of concentrates of PCH oxidations showed that several products could be separated. Investigation of these products by gas chromatography/mass spectroscopy (GC/MS) then showed that all were isomeric phenylcyclohexanes and phenylcyclohexanols, with no indications of C_{24} or C_{36} products. However, FIMS of the same concentrate showed that C_{24} and C_{36} products were present. These experiments suggested that in the future C_{12} products should be determined by GC/MS and that higher molecular weight products should be determined by a simpler FIMS technique.

Details follow. However, our gum determinations[2] appear to be a satisfactory substitute for all the methods mentioned above in semiquantitative comparisons of fuels.

4.2. Size Exclusion Chromatography

Work started with a sample of PCH that had been oxidized in air for 7.2 hours at 130°C. Size exclusion chromatography measurements were performed

with a 100 Å styragel column, tetrahydrofuran as solvent, and a differential refractive index (DRI) detector. The chromatogram of unoxidized phenycyclohexane shows a piincipal peak at a retention volume of 7.7 mL (7.7 min at a flow rate of 1 mL/min) and a subsidiary peak at 8.4 mL. Analyses of the oxidized sample contained the same two maxima, but in addition had a shoulder at 7.0 mL and a pronounced tail from 6 to 7 mL, indicating the presence of larger molecular weight species. The area under this tail amounts to ~10% of the total area of the chromatogram. The existence of species of varied chemical composition, revealed by the HPLC experiment to be discribed, and the lack of suitable molecular weight standards discouraged further use of this method. These results, however, eliminate the possibility of polymeric species with molecular weights >10,000 and indicate that the contribution of intermolecular addition reactions between unsaturated or polar sites is slight or absent.

4.3. High Pressure Liquid Chromatography

The first HPLC experiments were conducted with unoxidized PCH and a 20:1 concentrate of oxidized PCH on a C-18 reverse phase column equipped with DRI and UV absorption detectors. In neat acetonitrile, a single peak for the PCH was observed at a retention volume of the 3.7 mL with both detectors. For the oxidized sample, considerable broadening of 3.7-mL peak was observed. A small shoulder at 4.4 mL was found by both detectors.

To enhance the separation efficiency, we repeated the analysis in a 25 vol% solution of water in acetonitrile. Three major peaks and several minor ones were observed with the UV detector. Five major peaks were observed by DRI. There was little correspondence in retention volume among peaks found by the two detectors, probably due to the relatively weak DRI response. Our results suggest two conclusions:

(1) There are a number of readily separable species in the oxidized fuel. With minimal effort, nearly ten species have been located.

(2) The considerable chemical heterogeneity of the species results in elution at different times and markedly different DRI and UV responses.

These experiments were continued with 50 vol% of acetonitrile in water as the mobile phase. The 20:1 concentrates of the oxidation products were diluted with this solvent for injection, but the pure hydrocarbon was added in

75% acetonitrile. Analysis of unoxidized phenylcyclohexane (PCH) with the UV detector operating at 254 nm (Figure 10) shows peaks at retention volumes of 4.17 mL and 17 mL. The first peak is detectable by UV absorbance but not by DRI. Because the refractive index of the PCH (1.53) is sufficiently different from those of acetonitrile (1.34) and water (1.33) it should show up in both the DRI and the UV detectors. We have therefore assigned the 17-mL peak to PCH and regard the 4.17-mL peak as an inadvertent impurity.

Samples of PCH, oxidized for 4 as well as 7.2 hours, were used in these experiments after concentration by 20:1. The concentrations removed essentially all the PCH, as shown in Figure 10b and 10c. Oxidation produces six major peaks, four in a quartet at 2.17 to 3.42 mL and two more at 5.55 and 11 mL. All have greater polarity than PCH (17 mL) as determined by the decrease in retention volume on the C_{18} reverse-phase HPLC. As measured by the areas under the curves, the proportion of 5.5-mL material increases greatly between 4 and 7.2 hours, while the proportions of 11- and 3.1-mL materials show large decreases.

The concentrates of the 4- and 7.2-hour oxidations were then analyzed by GC/MS using a 1% SP2100 column with temperature programing from 100° to 300°C at 20°C per minute. The products included phenylcyclohexane (not detected by previous HPLC) and were very similar for both samples. Figure 11 shows the GC traces and assigns peak numbers. Table 1 summarizes the mass spectra of the GC fractions, listing first the parent peaks with the highest m/z numbers, then the m/z number for the four strongest peaks. Formulas of fragments of parent peaks are proposed, assuming that the phenyl group remains intact. (This assumption results in some groups that are very low in hydrogen content, leaving some possibility for loss of acetylene fragments from benzene rings.)

Peaks 11 and 12 both correspond to phenylcyclohexane but one must represent an isomer because they produce very different fragmentation patterns. Peak 13 corresponds to a phenylcyclohexene. The remaining four peaks correspond to isomeric phenylcyclohexanols, 1-, 2-, 3- and 4-, all of which can have cis- and trans-forms. Thus, both HPLC and GC have been successful in separating the major C_{12} products, but have given no identifiable C_{24} products.

To check the presence of C_{24} and C_{36} compounds in oxidized PCH, we oxidized another sample at 130°C for 5 hours and then concentrated by vacuum
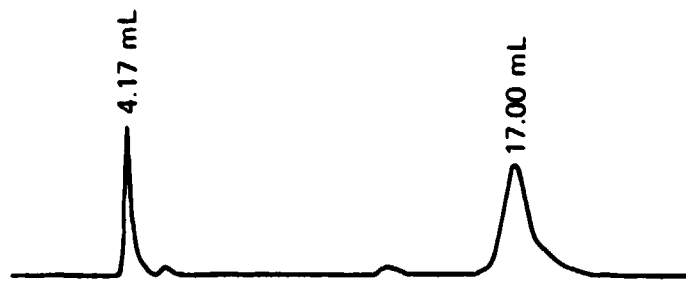
(a) Unoxidized Phenylcyclohexane
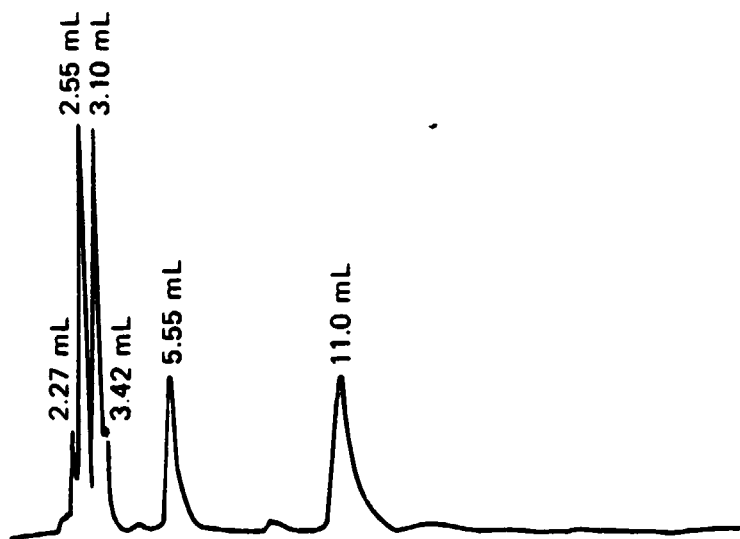
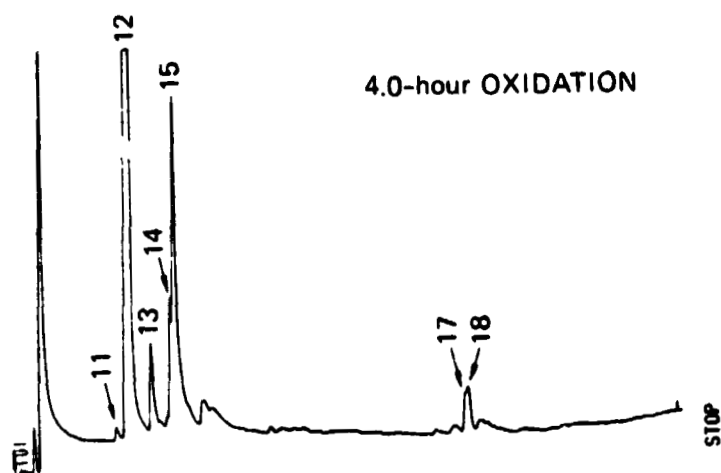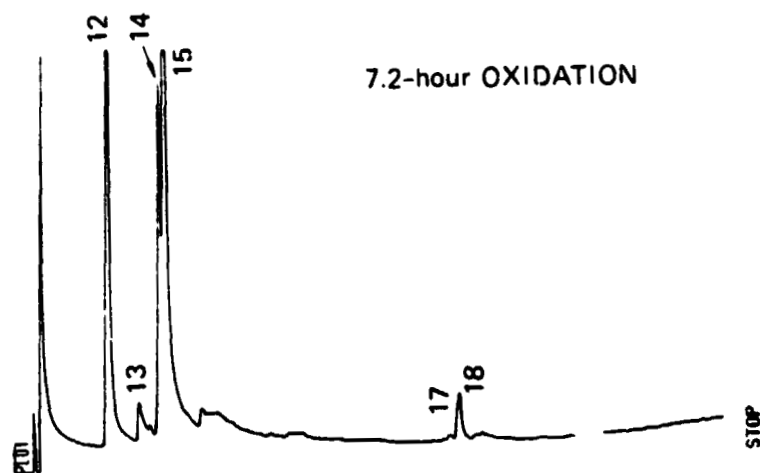(b) 4.0-hour Oxidation Products
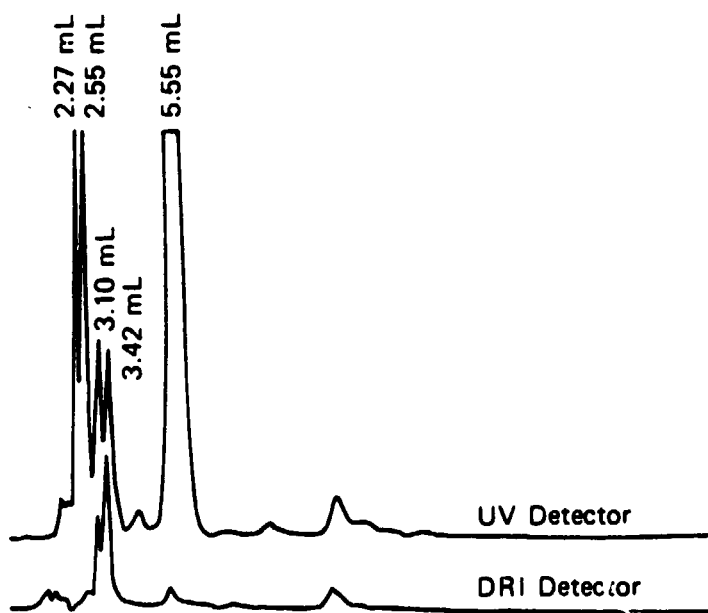
(c) 7.2-hour Oxidation Products

JA-2115-9

FIGURE 10   HPLC WITH UV DETECTOR OF PHENYLCYCLOHEXANE
AND ITS OXIDATION PRODUCTS

23

FIGURE 11   GAS CHROMATOGRAMS FOR OXIDATION PRODUCTS
OF PHENYLCYCLOHEXANE AT 130°C

JA-2115-10

24

Table 1

MASS SPECTRA OF GAS CHROMATOGRAPHY FRACTIONS

No.	Highest m/z, Parent Peak	Intensity	RANK OF IONS FOUND			
			1, strongest	2	3	4
11	160, Ph-C_6H_{11}[a]	Weak	145, Ph-C_5H_8·	91, Ph-CH_2·	118, Ph-C(Me)(CH₂)·CH₂	131, Ph-C_4H_6·
12	160, Ph-C_6H_{11}[a]	Strong	104, Ph-CH=CH_2	160, parent	117, Ph-C=CH_2	91, Ph-CH_2·
13	15_ Ph-C_6H_9[b]	Strong	158, parent	129, Ph-C_4H_4·	130, Ph-C_4H_5	115, Ph-C_3H_2
14		Weakest of group, few other peaks	105, Ph-ĊH-Me	120, Ph-i-Pr	77, Ph·	51, ?
15	176, Phenyl-cyclo-hexanol	Has most other peaks	133, Ph-C_4H_8·	105, Ph-ĊH-Me	120, Ph-i-Pr	176, parent
17		Strongest of groups, many other pea s	91, Ph-CH_2·	159, Ph-C_6H_{10}·	176, parent	133, Ph-C_4H_8·
18		Many small eaks	159, Ph-C_6H_{10}·	91, Ph-CH_2·	158, Ph-C_6H_9	176, parent

[a] Phenylcyclohexane.

[b] Phenylcyclohexene.

distillation to 1/273 of its oxidized weight. When this concentate was analyzed by GC/MS as described above, we found the same C_{12} products but no evidence of C_{24} or C_{36} products. Nevertheless, FIMS shows that the latter products were present.

Table 2 compares FIMS of the concentrate and of a comparable 5.5-hour oxidation of PCH with evaporation of the whole products in the FIMS.[11] Because losses during evaporation are poorly reproducibile, the products found are listed according to the rankings of their magnitudes. The results show first that the concentrate contains both C_{24} and C_{36} oxidation products, which GCMS did not detect. To reconcile results of the two concentration techniques, it appears that: (1) concentration by distillation cut out the phenylcyclohexane but retained more of the C_{12} oxidation products; (2) because more C_{12} oxidation products were retained, the proportions of C_{24} and C_{36} products in the concentrate must be lower; (3) different peak intensity patterns arose from different decompositions of peroxides during different heating conditions; (4) the FIMS evaporation must be unselective if considerable C_{12} hydrocarbons are retained while considerable C_{12} oxidation products are lost.

Table 2

FIMS ANALYSES OF OXIDATION PRODUCTS OF PHENYLCYCLOHEXANE AT 130°C

m/z	Probable Structure		RANK OF PEAK INTENSITIES	
			FIMS 34806, Normal Evaporation	FIMS 17001, Concentrated 273 to 1
159	R^+ from ROH or RO_2H		2	1
160	RH, $C_{12}H_{16}$		1	
172	Unsaturated ketone .			6
174	Ketone			3
175	RO^+			5
176	ROH		3	2
192	RO_2H		7	4
318	Dimer, $C_{24}H_{30}$ = R'H		None	
332	Dimer ketone		5	a
333	$R'O^+$		8	
334	R'OH		6	4
335	$R'OH_2$		9	
348	OH ketone		10	5
350	$R'O_2H$ or glycol		4	1
351	Glycol + H^+			2
364	R'H + 3 O - 2H			6
366	R'H + 3 O			3
476	Trimer, $C_{36}H_{44}$ = R"H		None	
504	R"H + 2 O	-4H	2[b]	2
506		-2H	1	
507		-H	3	
508		-no H	4	
520	R"H + 3 O	-4H		2
522		-2H	6	2
524		-no H		1[c]
540	R"H + 4 O		5	2

[a]Because the strongest dimer peak in 17001 had about half the intensity of the 172 peak, ranks below a apply to dimers only.

[b]This and lower ratings are for C_{36} compounds only. The strongest C_{36} at 506 had about half the intensity of the C_{24} peak at 348.

[c]The strongest C_{36} peak at 524 had one-fourth the intensity of the dimer peak at 364. The 504, 520, 522, and 540 peaks had the same intensities, slightly weaker than that for 524.

27

5. CONCLUSIONS

Our fuel oxidation studies lead to the following conclusions. Although diesel and jet fuels are mostly paraffins, the alkylbenzenes and more reactive components of the fuels do most of the reacting with oxygen, directly through attack of alkylperoxy radicals, and indirectly through attack of alkyl radicals. Even if they did oxidize extensively, the alkanes would not give much gum. Until their concentrations exceed ~1 M, these reactive alkylaromatic hydrocarbons will retard the oxidation of alkanes, but be capable of forming gum or deposits, perhaps nearly as well as the pure reactive hydrocarbons. These reactive hydrocarbons alone will have a wide range of rates of oxidation under standard conditions; their hydroperoxides will produce a wide range of rates of initiation; and their oxidation products will probably have a wide range of abilities to condense to gums and deposits.

This last property is probably the most important and least understood factor in gum formation and will receive major attention in the continuation of this program. We plan to investigate 10% tetralin/90% dodecane mixtures. The effect of oxygen pressure on gum formation will be checked and extended, and a correlation of gum formation and JFTOT tests will be initiated in collaboration with NASA-Lewis.

As for alternatives to FIMS for measuring precursors formation, we conclude that GCMS will provide good analyses for C_{12} products, when needed, but not for C_{24} and C_{36} products. However, if the oxidized sample is evaporated for a few minutes in the FIMS vacuum at room temperature, most of the parent hydrocarbon and monomeric oxidation products will be lost, and the least volatile dimers and trimers probably can be determined more accurately and quickly. However, it appears that our new method for determining gum[2] will be adequate for routine comparisons of fuels.

REFERENCES

1. S.E. Buttrill, Jr., F.R. Mayo, B. Lan, G.A. St. John, and D. Dulin, Oxidaiton and Formation of Deposit Precursors in Hydrocarbon Fuels, NASA Contractor Report 165534 (January 1982).

2. B. Lan and F.R. Mayo, Preliminary Report on Determination of Gum in Fuels, Apendix to Report No. 8 to U.S. Army Research Office, Contract No. DAAG29-80-C-0122 (October 1982).

3. F.R. Mayo, S.E. Buttrill, Jr., B. Lan, and G.A. St. John, Basic Study of Fuel Storage Stability, Interim Report No. 2 to U.S. Army Research Office, Contract DAAG29-80-C-0122 (April 1982).

4. J.A. Howard, Advances in Free Radical Chemistry, 4, 49 (1972).

5. G.A. Russell, J. Amer. Chem. Soc., 78, 1035, 1041 (1956).

6. F.R. Mayo and A.A. Miller, J. Amer. Chem. Soc., 78, 1023 (1956).

7. B. Lan, F.R. Mayo, and G.A. St. John, Basic Study of Fuel Storage Stability, Monthly Report No. 5 to U.S. Army Research Office, Contract DAAG29-80-C-0122 (July 1982).

8. G.A. Russell, J. Amer. Chem. Soc., 77, 4583 (1955).

9. V.S. Rafikova, I.P. Skibida, Z.K. Maizus, and N.M. Emanuel, Chem. Abstr., 70, 3011 (1969).

10. Ibid., 75, 62665 (1971).

11. F.R. Mayo, S.E. Buttrill, Jr., B. Lan, and G.A. St. John, Basic Study of Fuel Storage Stability, Interim Report No. 1 to U.S. Army Research Office (March 1982).