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OXIDATION AND GUM FORMATION IN DIESEL FUELS(U) SRI
INTERNATIONAL MENLO PARK CA CHEMISTRY LAB F R MAYO
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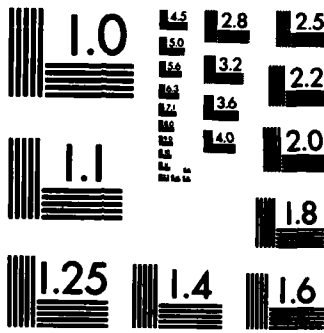
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report describes experiments on oxidation and gum and deposit formation from n-dodecane, tetralin, 2-ethylnaphthalene, and diesel fuels at 43°, 60°, 100°, and 130°C and discusses their implications. Techniques and precision of gum determinations are discussed. Some literature reviews by the author are summarized.		

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1. OBJECTIVES

The objective of this current one-year contract is to relate the oxidations of fuels at 130°C, where experiments can be performed in hours or days, to standard tests for fuel stability at ambient temperatures and 43.3°C (110°F), which require many weeks. Another objective is to prepare a manuscript for publication on our work on oxidations of fuels at 130°C, done mostly on previous ARO and NASA contracts. This manuscript has just been submitted to Industrial and Engineering Chemistry, Product R&D.

2. NEW DATA ON OXIDATIONS

This section summarizes new data on oxidation (2.1) and then presents our conclusions on this work (2.2).

Fuel 14 was chosen for many oxidation experiments because we had the most on hand. When it appeared to give large blanks without any oxidation, it was distilled in vacuum from a flask with a Vigreux neck. The original fuel distilled from 50° at 30 torr to 250° at 16 torr. Redistillation gave 92.5% of 14A, b.p.₁₄ 53-200° and 5.4% of 14B, b.p.₁₃ 200-234°C.

2.1. New Data

Table 1 summarizes data obtained since September 9, 1984, the starting date for the present ARO contract. The 130°C experiments were done to determine trends in rates with time for these important hydro-

Table 1

OXIDATION OF KNOWN HYDROCARBONS AND FUELS IN AIR

Expt. No.	Fuel ^a	Reaction Time	% Reaction of O ₂ ^b	R _O ^c	R _g ^d	R _g /R _O	% O ₂ ^e in RO ₂ H	Remarks
Oxidations at 130°C								
K80	DOD	2.03 h	12.0	7.55	1.16	0.154	14	Gum blanks are erratic and R _g is too high for 2h. Shows autocatalysis.
		4.0 h	44.5	13.0	0.38	0.029	50	Fairly steady R _g /R _O except at 2h. Increasing yields of RO ₂ H.
		6.0 h	77.4	14.7	0.27	0.018	60	
K81	TET	0.57 h	49.0	75	5.72	0.076	~100	Fairly steady rate, consistent R _g /R _O . High yield RO ₂ H.
		0.93 h	70.3	69	6.9	0.10	~100	Shows O ₂ depletion
		2.07 h	91.4	44.1	2.32	0.053	~75	
K86	EtN	0.50 h	33.4		22	0.34	63	Gum blank ~ 1.20
		1.0 h	36	64	42	0.66	60	Shows decreasing rate, erratic R _g , increasing R _g /R _O , inc. yield RO ₂ H.
		2.0 h	64	42	42	1.00	77	
C28	Fuel 14	58 h	8.5	0.77	0.30	0.39		From earlier ARO report. Film deposit at 7 h
L4A	Fuel 14A	72 h	19.3	0.220				Deposit at 72 h
		next 164 h	33.0	0.164	0.51 sol.			
		total 236 h		0.181	0.29 dep.	4.42	---	
L4B	Fuel 14B	72 h	28.4	0.42				
		next 66 h	31.2	0.50	3.97 sol.			
		total 138 h		0.46	0.94 dep.	11	---	Deposit at 72 h

Table 1 (Continued)

Expt. No.	Fuel ^a	Reaction Time	% Reaction of O ₂ ^b	R _O ^c	Oxidations at 100°C			Remarks
					R _g ^d	R _g /R _O	% O ₂ ^e in RO ₂ H	
K89C	DOD ^h	7	d	94	0.683	0.199	0.29	--
K89D	DOD + 0.0366M t-Bu ₂ O ₂	7	d	91	0.665	0.192	0.29	--
K92A	DOD	52	h	12	0.28			
		49	h	37	0.92			
		total	h		0.59	0.066	0.111	87
K92C	DOD + 0.041M t-Bu ₂ O ₂	23	h	52	2.63	0.26	0.99	67
K92B	DOD + 0.031M t-Bu ₂ O ₂	52	h	82	1.94	0.23	0.116	70
K89A	Fuel 14	7	d	4	0.029			
		7	d	4	0.025			
		14	d	7	0.022	0.0482 gum		Slowly decreasing rate
		28	d		0.025	0.0480 dep.	3.8	Faint film deposit
K89B	Fuel 14 + 0.037M t-Bu ₂ O ₂	7	d	54	0.35			
		6	d	25	0.18			
		7	d	18	0.13	0.621 gum		Film deposit present
		20	d		0.22	0.346 dep.	8 4.4	Steadily decreasing rate
LAC	14A + 0.010M t-Bu ₂ O ₂	72	h	12	0.180			
		7	d	12	0.073	0.305 gum		
		240	h		0.105	0.141 dep.	4.2	Decreasing rate
L4D	14A + 0.101M t-Bu ₂ O ₂	72	h	65	0.966			
		68	h	35	0.548	2.51 gum		
		140	h		0.763	0.89 dep.	4.5	Decreasing rate

Table 1 (Concluded)

Expt. No.	Fuel ^a	Reaction Time	% Reaction of O ₂ ^b	R _O ^c	R _g ^d	R _g /R _O	% O ₂ ^e in RO ₂ H	Remarks
Oxidations at 60°C								
K88A	Fuel 14	43	d	0.78 to 3.3	0.0103	0.0121	1.17	~ 3 No deposit noted
L11A	Fuel 14A + 0.20M t-Bu ₂ O ₂	14	d	4.5	0.0135			
	next	14	d	6.5	0.0053			
	next	14	d	10.6	0.0127			
	total	42	d		0.0107	0.0265	2.48	14
L11B	DOD	14	d	1.2	0.0045			
	next	14	d	1.8	0.0022			
	next	14	d	2.1	0.008			
	total	42	d		0.0025	0.015	5.9	16
L11C	DOD + 0.20M t-Bu ₂ O ₂	14	d	9.3	0.0336			
	next	14	d	14	0.0171			
	next	14	d	6.8	0.0250			
	total	42	d		0.0253	0.0068	0.27	76
Oxidations at 43.3°C								
K79	Fuel 14	0 weeks			1.70/0 ^f		0	
		2 weeks			2.06/336		~ 0	
		4 weeks			2.40/672		~ 0	
		8 weeks			2.64/1344		—	
		16 weeks			2.8/2688		<0.8 μmole/100 g fuel	
		24 weeks			4.7/4008		No deposit seen	

^a DOD = n-dodecane; EtN = 2-ethylnaphthalene; TET = tetralin.

^b Maximum depletion of O₂ in one or any one of several steps.

^c Average rate of O₂ absorption in μmoles O₂/g fuel·h.

^d Average rate of gum formation in mg gum/100g fuel·h.

^e % of O₂ absorbed found by titration as hydroperoxide.

^f First number for each time at 43° is mg gum/100g fuel; second number is time in hours.

^g Partly soluble in acetone, but readily soluble in equal volumes of EtOH, AcMe, and C₆H₆.

^h The DOD used in K89C and all subsequent DOD runs was previously washed with conc. H₂SO₄ and water and then

carbons. The remarks call attention to differences among fuels.

Generalizations are developed in the next section 2.2.

2.2. Summary and Conclusions

→ Rates of oxygen absorption (R_o) and gum formation (R_g) are defined in Table 1 and are now related by the R_g/R_o ratio, the reciprocal of the ratio previously used. The change was made because when the oxygen content of the gum is known, the R_g/R_o ratio is proportional to the fraction of oxygen absorbed that appears in the gum.

According to Table 1, oxidations of tetralin (TET) and 2-ethylnaphthalene (EtN) at 130°C are initially fast but the rates decrease regularly. The oxidation of n-dodecane (DOD) is clearly autocatalytic; it requires the most oxygen to produce a milligram of gum while EtN, among the pure hydrocarbons, requires the least. Rates of oxygen absorption for DOD at 100°C appear to be erratic. Part of the problem is autocatalysis; part is near exhaustion of oxygen. The best results are those for K92A and K92C. R_o without t-Bu₂O₂ is autocatalytic. 0.041M peroxide increases R_o by 4.46 times but has little effect on R_g/R_o . Oxidations of DOD are much slower at 100°C than at 130°C and still slower at 60°. The latter oxidations are accelerated tenfold by 0.2M t-Bu₂O₂. R_o and R_g/R_o are unreasonably high for L11B.

→ Trends in oxidations of Fuels 14 and 14A, which are different at 130°C, are not yet clear at 100°C and 60°C. Further experiments at 60°C will be done with Fuel 14A and a faster oxidation initiator, ABN (2,2'-azobisisobutyronitrile). Up to 24 weeks, oxidations of Fuel 14 in partly closed bottles at 43°C produced gum at an initial rate of 0.0010

mg/100 g fuel·h (corrected for the blank at zero time), with some tendency for this rate to decrease. No deposits have appeared.

Oxidations of Fuel 14 gave fairly homogeneous dark films on the part of the Pyrex vessel at 100° and 130°C that was in contact with the fuel. There were no other solids at reaction temperature, but a faint cloudiness appeared on cooling the reaction mixtures. We interpret this cloudiness to decreasing solubility of the deposit in fuel and we count it as soluble gum. We think that the continuous mild shaking of our reactor causes all the deposits to grow on the surface films. The ratio of insoluble/soluble gum with $t\text{-Bu}_2\text{O}_2$ in Experiment K89A, ~ 1 , is the largest that we have seen.

As indicated at the beginning of Section 2, Fuel 14 was fractionated into lower (14A) and high boiling (14B) fractions. The higher-boiling 14B absorbed oxygen 2-3 times as fast as 14A and gave gum and deposits about 6 times as fast. The result is that 14B requires only 41% as much oxygen to produce a milligram of gum. FIMS analyses that might account for these differences are in progress. Experiments L4C and L4D show the effects of 0.010 and 0.010 M $t\text{-Bu}_2\text{O}_2$ on the oxidation of 14A at 100°C. The initial R_0 is increased by a factor of 5.37 and total R_g by a factor of 7.62. These factors correspond to reactions of 0.726 and 0.875 order on $t\text{-Bu}_2\text{O}_2$, respectively. However, the rates of both reactions decrease with increasing reaction time and the final average R_g/R_0 ratios are the same.

Table 1 gives some yields of hydroperoxides on the oxygen absorbed. The best yields are associated with the fastest oxidations, but it is also clear that initially EtN hydroperoxide does not survive as well as

TET hydroperoxide, but may therefore be a better initiator. DOD hydroperoxide is the least stable, especially during the induction period, but may be the fastest initiator of the group.

→ The important points in the above discussion are:

The oxidation of DOD is autocatalytic; oxidations of TET, EtN, and Fuel 14 are self-retarding.

In our oxidations of Fuel 14 with shaking, all the deposits at 100^f and 130^d°C appear as films on glass; no deposits have yet been obtained at lower temperatures.

The ratio, B_g/R_o^{put} , still appears to be essentially constant for any fuel at a single temperature, even with large differences in B_o^{put} from addition of t-Bu₂O₂. Thus, gum can be accumulated relatively rapidly for experimental purposes.

We are accumulating new data at 43^f and 60^f°C. These findings should assist materially in our efforts to understand and devise a test for fuel stability.

3. GUM DETERMINATIONS

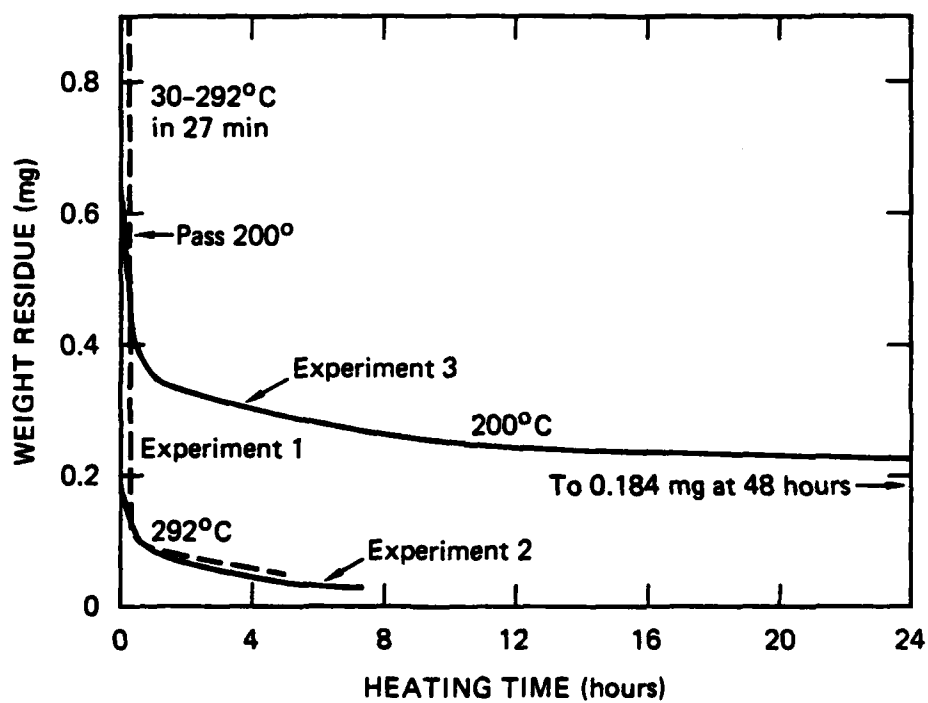
Gum has been determined by the method in the next paragraph, finally heating at 200°C in a slow stream of nitrogen to "constant weight" in about 20 hours.

In an effort to improve our understanding of this method, thermogravimetric analyses (TGA) were performed in nitrogen with a DuPont 951 Thermogravimetric Analyzer coupled to a DuPont 1090 Thermal Analyzer. Each of three experiments was performed with 3.35 g (4 mL) of Fuel 14, aged 16 weeks at 43°C. Each sample was evaporated nearly to dryness in

a small vertical furnace that had an equilibrium temperature of 300°, but the fuel temperature was controlled by evaporation of fuel and a stream of nitrogen through a capillary, enough to make a depression in the fuel surface but not enough to cause spattering. Each residue was transferred with 1-2 mL of reagent acetone to a tared aluminum dish 25 mm in diameter and weight ~53 mg and evaporated to dryness on a warm hot plate. The samples had different initial weights at this point but presumably contained the same amounts of gum. These dishes were then rolled into cylinders and examined by TGA in a nitrogen atmosphere. Weight changes are summarized in Figure 1 and some details are provided in Table 2.

It is clear that there is no equilibrium or constant weight at either 200° or 292°C and that much more weight is lost at 292°C. In view of the differences in the initial heating of the two 292° experiments, they are good checks.

The following is a reasonable explanation of the results but I do not claim that it is original. By analogy with some polymerization processes, there should be more moles of fuel dimer (2 fuels molecules and 0 to 2 oxygen molecules) than any other oligomer and decreasing molar proportions of trimers, tetramers, etc. Most of the monomeric fuel oxidation products were removed before TGA started. From their volatilities, the dimers are lost fastest, and so on. Pyrolysis of gum, especially peroxides, may contribute to the weight loss, but most of the least stable products should be lost in the first evaporation above 200°C.



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FIGURE 1 WEIGHT CHANGES OF GUM SAMPLES FROM 30°C TO 200°C OR 292°C

Table 2
DETAILS FOR TGA EXPERIMENTS IN FIGURE 1

Experiments	1	2	3
Initial weight, mg	2.116	0.677	0.822 ^a
First weight at temp., mg., °C	0.106, 292	0.473, 292	0.639, 200
Final weight, mg	0.051	0.039	0.184
Mg gum/100 g fuel	1.52	1.16	0.550

^a0.791 mg after standing with conc. H₂SO₄ and mineral oil at 13 torr for 4 days.

Theoretically, a sharp cutoff between monomeric and dimeric products would be desirable. Practically, a cutoff between dimeric and trimeric products might be more useful if dimers contribute least to engine deposits. On the basis of Experiment 3, recent gum determinations have been made after about 20 hours of heating at 200°C, partly because this time is convenient and partly because it corresponds to most of our earlier gum determinations. The difference between heating for 16 or 24 hours is hardly significant; residue weights are changing by 1% per hour.

The absolute values of our gum determinations are of dubious significance. However, the gum contents are assumed to provide valid comparisons of gum contents. By use of data for oxidation, Experiment K89A with Fuel 14 during 28 days at 100°C and Experiment 3 in Figure 1, some educated guesses can be made about the extent of gum formation. Fuel 14, normalized to 100 g, absorbed 1.65 mmoles, 52.8 mg of oxygen

and gave about 90 mg of dimers and higher oligomers and then 32.4 mg of "gum" after heating for 20 hours at 200°C. This "gum" contains 0.03% of the original carbon in the fuel and about 8% oxygen, 2.67 mg, 5.1% of the oxygen absorbed. This experiment also yielded a black film on the Pyrex flask. The film was thoroughly rinsed with hexane and then extracted with an acetone/ethanol/benzene mixture. After evaporation of this solution and drying at 1 torr, the deposit weighed 32.24 mg; it was not heated. That 5% of all the oxygen absorbed appeared in the final gum and probably another 5% in the deposit, even after significant losses at 200°, is surprising. These results suggest that much of the oxygen absorbed by the best gum-forming fuels may go directly into gum.

Our evaporation technique in gum determination has been tested by using the oxidized Fuel 14A from Experiment L4A. Four pairs of evaporations were performed with 2-3.5 g samples of fuel: (1) evaporation to a 6-mm circle of liquid, (2) evaporation to dryness (no flow), (3) evaporation to dryness and then for 10 minutes longer, and (4) by vacuum distillation. In the last procedure, the fuel was concentrated almost to dryness at 1 torr. A cold finger containing dry ice was then inserted and the distillation was continued to dryness, all parts of the distilling flask being heated to about 100°C. This procedure is expected to remove all monomeric products. The residue was then transferred to the usual aluminum dish with reagent acetone. Although the first weights of the four dishes before heating varied considerably, the final weights of the residues after 20 hours of heating all fell between 118.6 and 124.7 mg/100 g fuel and averaged 121.2. Thus, for large residues (4 mg on the dishes), the differences among these evaporation procedures are insignificant and reproducibility is excellent.

When blank determinations on unoxidized EtN seemed high, several blanks were run. The results with recently vacuum-distilled EtN in the order obtained were in mg/100 g fuel: 1.23, 1.61, 3.16, 1.09, 1.22, 1.35, average of 4 lowest results, 1.22. This average corresponds to 0.049 mg of gum from 4 mL of EtN. Thus our gum method becomes less reliable for low proportions of gum and some appears to be formed during the determination. As might be expected, attempts to improve gum determinations with low-gum samples gave erratic results.

Recent ideas on the mechanism of gum formation are presented in a manuscript submitted to Industrial and Engineering Chemistry (Section 4.3) and also to some recipients of this report, and are therefore not included here.

4. LITERATURE REVIEWS AND PUBLICATIONS

4.1. Preparation and Revision of Interim Report 1

During the current contract, I reviewed one chapter in the book by E. T. Denisov and G. I. Kovalev, "Oxidation and Stabilization of Jet Fuels". That chapter dealt with the effects of metal and alloy surfaces on rates of oxidation and gum accumulation from jet turbine fuels. My review was issued as Interim Report 1 and was dated November 16, 1984. The important conclusion was that the effects of metal surfaces on rates of oxidation and gum formation of a single fuel are small to moderate, much less than the differences that we find among different fuels at SRI. Therefore our proposed investigation of the effects of metals on gum deposit formation has a lower priority. However, metal surfaces and

dissolved metals may have important effects in the conversion of soluble gum to hard deposits.

These conclusions are unchanged but correspondence with Professor Denisov since issuance of my report shows that some revision of my report is desirable for the record.

In the second paragraph of the Background section, it should be noted that oxygen absorption rates are initial rates in 5-hour oxidations at 150°C where the oxygen was nearly completely consumed. The comparison of initial rates and final gum is therefore questionable.

Under the Results section, the last two sentences in the first paragraph should be replaced by: Although for most metals, the total gum formation increases linearly with the initial rate of oxygen absorption, Denisov thinks that this relation is purely empirical and that a kinetic explanation is difficult. It may be that in the metal-fuel combinations that react fastest, the most time is available for the oxidation products to form gum.

In the Conclusions section of Interim Report 1, delete the first two paragraphs and Figure 1.

4.2. "Distillate Fuel Storage Stability"

Dr. George H. Lee of the San Antonio Laboratory recently sent me copies of Summary Reports 1 and 2 of the above title, issued by the Wester Petroleum Refiners Association in 1958. I wrote to Dr. Lee at length about reactions to the Report and my conclusions are summarized here.

My review indicates that several unknown factors affect the rates of oxygen absorption of fuels and the accompanying gum formation. Rate data are hard to interpret, especially with fractions and blends. Nothing is said about reproducibility. Poor reproducibility is not surprising with spontaneous oxidations without added initiator. Perhaps a very small initial concentration of short-lived initiator will reduce differences among induction periods without altering basic differences among fuels. However, correlating and explaining moderate variations in rates of oxygen absorption of practical fuels and their fractions may not be worth the large effort that would be required. The main remaining fuel stability problems appear to be predicting fuel stabilities and the transitions of soluble gums to hard deposits on high engine parts.

Predicting fuel stabilities appears to be the more urgent problem; it has two parts. One is relating results obtained fairly quickly above 100°C to those at 43.3°C (110°F), close to storage temperatures where several months are required for tests. The other problem is quantitative measurement of gum. The conventional steam jet gum test is not adequate. The SRI test is better but some blanks are inacceptably high and duplicate results often disagree by 20% or more. The present status of our gum determinations is discussed in Section 3.

4.3. Gum and Deposit Formation from Jet Turbine and Diesel Fuels at 130°C

A long manuscript of the above title has been submitted to Industrial and Engineering Chemistry, Product R&D, to ARO, and to the

Army Laboratories at Fort Belvoir and San Antonio. This manuscript includes fuel stability research at 130°C at SRI International from September 1980 until now on diesel and jet turbine fuels, supported by ARO and NASA, respectively. Work has started on another manuscript dealing with oxidations at 100°C.

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Mr. Mark A. Featherstone carried out the thermogravimetric analyses.

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