Effect of Oxygen Concentration on the Thermal Stability of Naphthenes

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In connection with the possible use of hydrocarbons as fuels for hypersonic aircraft, investigations are being made on the thermal stability of prototype fuels at temperatures up to 1000°F. The presence of oxygen has a deleterious effect on the observed thermal stability, as measured by a high temperature coker, even at concentrations in the sub-ppm region. After developing a GLC method for determining oxygen in hydrocarbons down to 10 ppb, the effect of O_2 was explored with decalin at concentrations down to the level of detection. No effect was noted at O_2 concentrations up to ca 3 ppm but thereafter it was found that thermal stability decreased rapidly with increasing equilibrium oxygen concentration in the range up to about 10 ppm, more slowly up to about 15 ppm, and showed little subsequent response up to the saturation limit (ca 300 ppm). Methylcyclohexane and a naphthenic jet fuel were not investigated as completely but demonstrated somewhat similar but individual behaviors. It appears that the depositing tendency of the fuel is generally related to the basic kinetics of the oxidation of hydrocarbons but the reasons for the idiosyncracies of individual hydrocarbons are obscure.

Introduction

ALTHOUGH the thermal stability of aviation jet fuels has been studied for years, it is a subject of growing importance with the increase in flight speeds. Commercial sustained flight speeds in the region of Mach 3 are just around the corner, aircraft designers are actively contemplating increase into the Mach 6-7 region, and the Air Force is thinking of still higher flight speeds.[1] At high Mach numbers the utilization of the fuel to provide cooling for the engines and sensitive areas of the aircraft becomes more and more critical, involving not only sensible and latent heats, but also endothermic reactions as well. With the demands on the fuel becoming more severe, continuing research on the response of hydrocarbons to such conditions is needed. Among the factors of importance are 1) the structure of the hydrocarbons themselves, 2) the effect of trace components and contaminants (particularly metals), and 3) the effect of oxygen on degradation reactions. Various investigators have reported the effect of oxygen on the thermal stability of jet fuels,[2–6] but not particularly with regard to specific pure hydrocarbons, high temperatures, or to dissolved oxygen concentrations below about 1 ppm. In this paper, we report our work on two naphthenes, methylcyclohexane (MCH) and decalin, and on a high naphthene content jet fuel (RAF-163-60), where dissolved oxygen concentrations ranged from air saturation down to the ppb level. Descriptions of the fuels are shown in Table 1.

Experimental

It is necessary to describe first the experimental apparatus, which has to do directly with the thermal stability measurements and secondly, the analytical method used for dissolved oxygen determinations. Thermal stabilities reported in this paper were determined using the SD/M-6 fuel coker,[7,8] which has been modified to permit constant equilibration with a sparging gas of controlled oxygen content.

The SD coker is quite similar to the CRC coker, and consists essentially of an annular preheater, internally heated, and a heated sintered metal filter across which the pressure drop is measured. The inner tube of the heat exchanger is removable for observation of deposits. Flow is maintained at 6 lb/hr, but the SD coker is normally operated on a recycle regime, and the sample size has been reduced to 150 ml. Other design details and modifications have been described in earlier papers.[1,2]

For fuels and operating conditions such as used in the present work, vaporization usually takes place in the preheater, the vapor then passing through the filter (usually without significant pressure drop), cooling and condensing in a water cooled heat exchanger, finally passing through a Grove pressure regulator and back into the glass reservoir for recycle. The SD coker was operated at temperatures up to 900°F, usually at 250 psig. Preheater tube deposit ratings were judged in an Eppi Tuberator, using an extended color

Table 1 Fuel descriptions

Fuel properties

Fuel	Mole weight	Density, g/ml	Boiling point, °F	Critical temp., °F	Critical press., psi
Methylcyclohexane	98.2	0.769	213.8	574.7	504
Decalin	138.3	0.872	370.4	772.1	422
Jet fuel RAF—163-60	190[a]	0.863	396–504[b]	831[a]	402[a]

Fuel compositions

Fuel	Naphthene purity, %w	Naphthene conc., mole/l	Sulfur, ppm	Copper, ppm
Methylcyclohexane	100[c]	7.8	<0.2	<0.02
Decalin	100[d]	6.3	2	...
Jet fuel RAF—163-60	90[e]	4.5[a]	40	<0.02

[a] Properties estimated using the paraffin/naphthene split, UOP characterization factor, 100°F kinematic viscosity, and API gravity.

[b] ASTM D86 distillation; 50% point = 450°F.

[c] MCH contained trace amounts of cyclohexane and unidentified heavy ends, but was passed through a silica gel column prior to use.

[d] 91.2% trans-isomer; contained 0.1% Ionol as received, which was reduced to <1 ppm by passing over silica gel.

[e] Mass spec. analysis: 11% paraffins; 2% olefins; 15% 1-ring, 51% 2-ring, 18% 3-ring, 3% 4-ring naphthenes.

Received May 11, 1970; revision received October 16, 1970. This work was done under Air Force Contracts AF 33(657)-11096 and AF 33(615)-3789. We are happy to acknowledge useful discussions with Wright Field personnel, particularly H. R. Lander, Project Engineer, and excellent assistance in the laboratory by T. D. Sexton.

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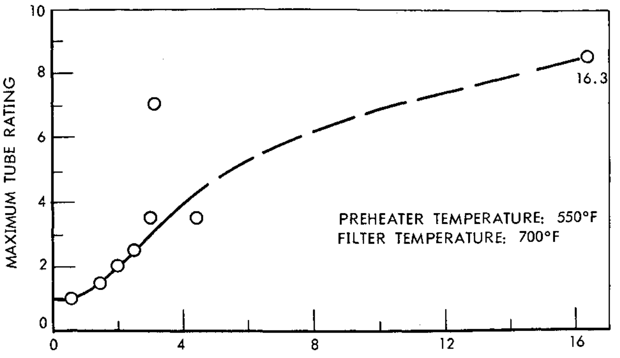

Fig. 1 Effect of dissolved oxygen on MCH thermal stability; averaged data points.

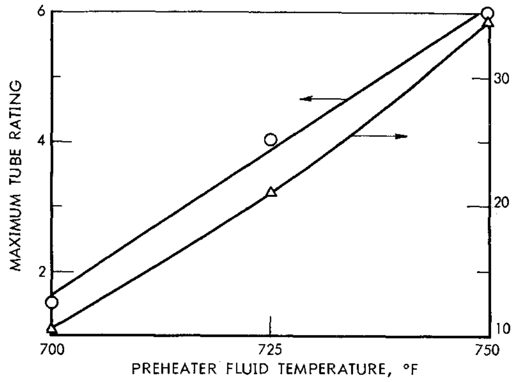

Fig. 3 Effect of temperature on thermal stability of decalin; 0.6 ppm dissolved oxygen; averaged data points.

code scale (8 max), for each inch of tube. The maximum rating is, of course, the greatest value observed at any area on the tube, while the total rating is the sum of all 13 areas. In some instances total as well as the maximum ratings are given.

To vary the dissolved oxygen content of the test fuels, several gas supplies of fixed and known oxygen concentration were previously prepared by suitable partial pressure blending of pure oxygen and nitrogen in standard nitrogen cylinders. Accurate O_2 concentration measurements were then made chromatographically.

Prior to beginning a run, the fuel was thoroughly sparged with the proper equilibrating gas. Simultaneously, the coker was flushed for at least an hour with a large flow of nitrogen. Since the SD coker was used in a fuel recycle mode, dissolved oxygen was continuously diminished by reaction in the test section, but the fuel was resaturated by gas sparging in the fuel reservoir. Saturation was ensured by following the dissolved O_2 content of the fuel effluent from the reservoir while increasing the sparge gas flow until the dissolved oxygen concentration no longer increased with further increase in gas flow rate. After the run was started and the test sections had reached thermal equilibrium, the reservoir oxygen content was again checked, and the sparge gas flow further increased, if required, to maintain equilibrium dissolved oxygen concentration. Where dissolved oxygen levels below 100 ppb were desired, helium was used as the sparge gas (O_2 ca. 6ppm).

Dissolved oxygen determinations were made using a chromatographic technique similar to that of Elsey,[9] utilizing a $\frac{1}{4}$-in. × 10-ft column of 60/80 mesh, 5A molecular sieve, and a thermistor type detector. Although base line stability becomes limiting at high sensitivity, dissolved oxygen detection at concentrations below 50 ppb was found possible. Readout was on a 1 mv recorder, and peak areas were determined by integrator count, or by planimeter; the latter method is favored for better precision at low oxygen levels. Oxygen was easily resolved from nitrogen since the ratio of emergence times (N_2/O_2) was about 3. To make a dissolved oxygen determination, a liquid hydrocarbon sample of up to 1 ml was injected into a Vigreaux column, where helium carrier gas quickly removed the air from the liquid.

Calibration of the analyzer was accomplished by using 1–10μl samples of hydrocarbon of known dissolved oxygen content. Such standard solutions were obtained by saturating liquid samples at a known temperature. A serious side problem involved was the danger of contamination with air in sampling and transferring. Even the tip of the hypodermic needle must not be allowed to come in contact with air, particularly when measuring dissolved oxygen concentrations below 1 ppm. In the figures, the preheater code ratings represent averaged values of two or more replicate determinations per set of conditions. Repeatability of coker ratings was generally within ±1 for maximum code, and to within ±5 for total ratings. Dissolved oxygen determinations were repeatable to within 5% above 1 ppm. At lower levels the error was greater, partly because of the great difficulty of avoiding adventitious contamination on sampling.

Discussion

In determining the effect of oxygen on fuel deposition tendency, a series of runs was made at a selected set of conditions, with various oxygen contents. The first two figures are typical of the type of data that were obtained. Figure 1 shows that at 550°F, methylcyclohexane (MCH) is most responsive to O_2 in the range from 1–4 ppm, becoming less so at higher values. The true rating at 16.3 ppm is uncertain, since the color was a heavy code 8, the upper limit of the scale. Also the possibility exists that the curve should sweep sharply upward at about 3 ppm, since, at the moment, we have insufficient data to known whether the point at 3.1 ppm

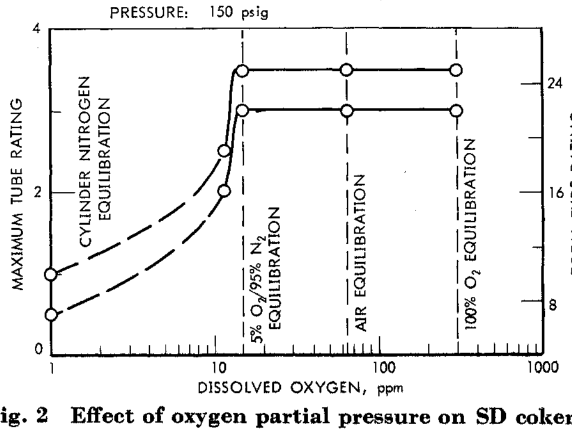

Fig. 2 Effect of oxygen partial pressure on SD coker preheater tube ratings of decalin; averaged data points.

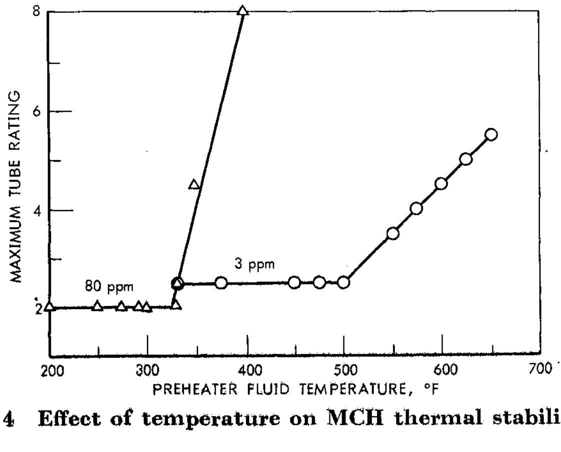

Fig. 4 Effect of temperature on MCH thermal stability.

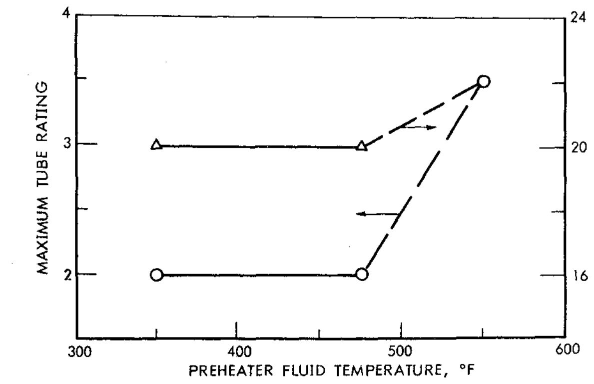

Fig. 5 Effect of temperature on thermal stability of decalin; 64 ppm oxygen; averaged data points.

is high or the point at 4.4 is low. However, in coker ratings at low O_2 contents it is easier to err towards higher ratings.

In Fig. 2, we see that the thermal stability of Decalin at 550°F remains constant over the entire range of 15–300 ppm oxygen, which corresponds to equilibration with gases of increasing oxygen-content-in-N_2 from 5%–100%. Below about 15 ppm, improvement in thermal stability is marked, but tends to level out towards 1 ppm, as shown further in Fig. 7. A critical concentration region exists between about 4 and 14 ppm. Figure 3 shows the large temperature gradient effect on Decalin when the dissolved oxygen content is only 0.6 ppm.

With good control of oxygen concentration, pure hydrocarbons demonstrate a sharp deposit-temperature breakpoint. This is illustrated by the behavior of MCH, shown in Fig. 4, for two oxygen concentrations. The breakpoint for MCH is increased from 325–500°F by reducing the dissolved O_2 content from 80–83 ppm. The divergent slopes of the curves demonstrate the fact that oxygen content becomes increasingly important as the temperature rises. At and below the air-saturation breakpoint (325°F, 80 ppm), oxygen concentration is of little importance. It would appear from this that there would be little to be gained from controlling O_2 content during flight with subsonic aircraft; but with supersonic, and particularly with hypersonic aircraft, handsome dividends would ensue from rigorous removal of O_2 from the fuel prior to take off.

In Fig. 5 a similar sharp breakpoint is shown for Decalin, even at air saturation conditions. This is a temperature effect; the previous breakpoint shown for Decalin was at constant temperature and was due to oxygen concentration change. In contrast to these sharp breakpoints, the naphthenic jet fuel displays a gradual change in deposit tendency with temperature (Fig. 6) which may be characteristic of hydrocarbon mixtures. This broader breakpoint may be related to the existence of a spectrum of reaction rates and mechanisms. Differences in sharpness of breakpoint have also been noted by Zengel.[10]

From Table 2 we can see how Decalin can be increased in thermal stability by 200°F by reducing the dissolved O_2 level from 64 down to 0.6 ppm. The improvement for MCH was 175°F, and with the RAF jet fuel, about 275°F. These are all O_2 reductions from approximate air saturation levels. As exposure to temperature is increased, the level to which O_2 may have to be reduced is indicated by the curves shown in Fig. 7 for all three fuels.

Table 2 Improvement in SD coker ratings by dissolved oxygen reduction

Fuel	Dissolved oxygen, ppm			$T_{2.5}$ breakpoint,[a] °F		
	High	Low	Δ	High	Low	Δ
MCH	80	3	77	325	500	175
Decalin	64	0.6	63.4	500	700	200
Jet fuel	40	0.4	39.6	500	775	275

[a] $T_{2.5}$ breakpoint temperature is the temperature at which the ASTM deposit code rating equals 2.5.

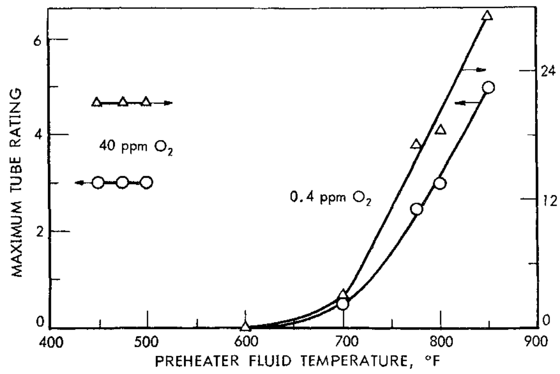

Fig. 6 Effect of temperature on thermal stability; 90% naphthene jet fuel.

The response of the Naphthenic jet fuel, although uncertain in the interval 500–725°F, shows increasing thermal stability with decreasing O_2 content up to the lowest level tested. At higher O_2 contents, its stability falls below that of Decalin. Mass spectrometric analysis of the jet fuel revealed that it contains a broad spectrum of 1, 2, 3, and 4 ring cyclics. The possible significance of this on its behavior is discussed later.

It is interesting to consider the effect of oxygen concentration in the light of our previous efforts[1,2] to tie the deposit forming reaction to the initial reaction of oxygen with hydrocarbons. If the initial reaction is assumed to be the interaction of a free radical with a dissolved oxygen molecule, leading to the formation of a chain propagating peroxide, the disappearance of O_2 may be represented by[11]:

$$\text{Rate} = -dO_2/dt = k_a(\text{RH})(\text{ROOH})/\{1 + [k'(\text{RH})/P_{O_2}]\} \quad (1)$$

where (RH) is the hydrocarbon concentration, (ROOH) is the concentration of peroxide formed, P_{O_2} is the partial pressure of oxygen, and k_a and k' are empirical constants. Under our conditions, (RH) is substantially constant for each hydrocarbon and will be approximately 7.8 for MCH, 6.3 for decalin and about 4.5 for the jet fuel (moles/liter).

Under high oxygen concentrations the partial pressure of oxygen could be relatively large and the rate expression would tend to approach

$$\text{Rate} = k_a'(\text{RH})(\text{ROOH}) \quad (2a)$$

or

$$\text{Rate} = k_a''(\text{ROOH}) \quad (2b)$$

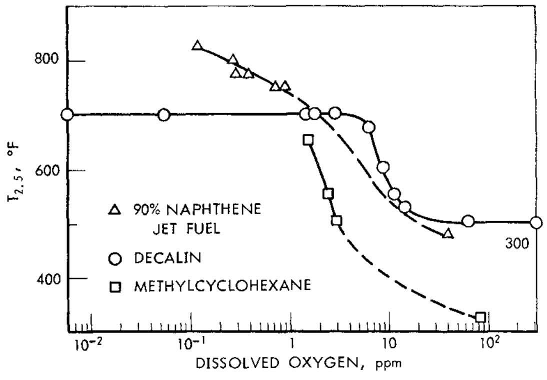

Fig. 7 Effect of dissolved oxygen on thermal stability of naphthenes; $T_{2.5}$ is the temperature at which the coker tube maximum rating is code 2.5.

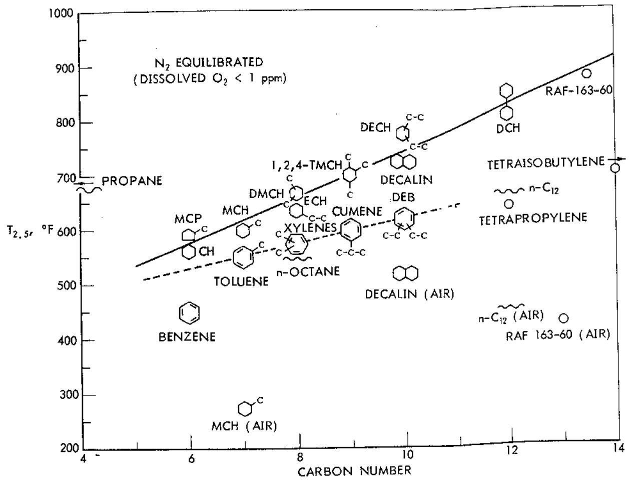

Fig. 8 SD coker break points ($T_{2.5}$) for naphthenes, paraffins, and aromatics; pressure = 250 psig.

being proportional to the peroxide concentration for any particular hydrocarbon. On the other hand at very low oxygen concentrations the expression would approach

$$\text{Rate} = k_a'''(\text{ROOH})P_{O_2} \tag{3}$$

If the assumption we made regarding the role of the initial oxidation reactions is valid, then the results we have obtained are in general agreement with this thesis. For instance, at high concentrations of oxygen the tendency to form deposits appears to be independent of O$_2$ partial pressures [following Eq. (2a)] while as the oxygen content is lowered, the rate (deposit tendency) decreases [following Eq.(3)] i.e., higher $T_{2.5}$ values.‡ Also, rates would be expected to decrease with increasing molecular weight for similar type compounds since they have lower molar concentrations. However, the tendency to form peroxides would be very important, also.

The failure of Decalin to follow the expected behavior below 3 ppm suggests that another mechanism, independent of oxygen content, is coming into play. Why this should be true for Decalin at this particular oxygen concentration, but not true for the jet fuel, can only be conjectured at the present time. It is remarkable that the naphthenic jet fuel proved to be more stable than Decalin at low oxygen concentrations, since the jet fuel undoubtedly contains C_5-, as well as C_6-ring naphthenes. The C_5-rings have been found to be less stable than the C_6- under conditions where substantial amounts of oxygen are present,[1,2,8] This may not be true under low oxygen conditions. It may be that each compound has a characteristic temperature at which it becomes indifferent to decreasing oxygen content, as suggested by the behavior of Decalin. When the fuel consists of a large number of compounds, as does RAF 163, the threshold temperature will gradually rise with decreasing O$_2$ as successive compounds abandon their dependence on oxygen concentration. In this case, it would be expected that at still lower oxygen levels the jet fuel would also become indifferent to changes in this parameter. It might also be expected that the proportion of oxygen in the deposits would decrease. Another expectation would be that comparable behavior could be achieved by a mixture of pure components. Both of these expectations will be tested in future work. It will be interesting to observe if such mixtures display synergy.

We have previously reported the effect of structure on the thermal stability of a wide variety of compounds.[1,2] We summarize this and additional subsequent data in Fig. 8 which show the results of a large number of tests at about 1 ppm O$_2$ with the breakpoint temperature plotted against carbon number. The data reveal that naphthenes are generally more stable than aromatics or paraffins of comparable molecular weight and that thermal stability increases with carbon number (and so also with molecular weight and, generally, with boiling point). The greater stability of naphthenes over aromatics is surprising, and it will be relevant to determine if this persists at very low O$_2$ concentrations. In the ultimate utilization of naphthenic fuels for cooling high speed aircraft the naphthenes will be catalytically dehydrogenated to aromatics (and H$_2$). Under these conditions the oxygen concentration will be vanishingly small. We have now constructed and are testing equipment which will measure the stability of aromatics/H$_2$ under near realistic conditions.

Conclusions

The thermal stability of naphthenes is strongly dependent on oxygen concentration, being independent at high levels, improving with decreasing content at intermediate levels (1–10 ppm) and then becoming indifferent again at low levels. Complete removal of oxygen increases the thermal stability breakpoint by about 200°F. At constant O$_2$, thermal stability increases with molecular weight and sometimes with mixture complexity.

Naphthenes are generally more stable than aromatics or paraffins of comparable molecular weight. Dissolved oxygen content, which has been of little importance to thermal stability with subsonic jets, may have to be rigidly controlled in fuels for future hypersonic aircraft.

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‡ $T_{2.5}$ is the temperature at which the coker tube rating is about midway between an ASTM code of 2 and 3.