The Role of Sulfur in the Thermal Stability of Jet Fuel

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ABSTRACT

The autoxidation of Jet A, dodecane, and a dodecane-15%-cumene blend doped with sulfur compounds were studied at 433 K. Oxygen, hydro peroxide and soluble gum were monitored during the autoxidation. Dodecane, cumene, and the dodecane-15%-cumene blend autoxidized rapidly, while Jet A had an induction period followed by a relatively slow post autoxidation. The results suggest that an inhibitor formed early in the post autoxidation of Jet A. Gum formed in the autoxidation of Jet A, whereas none was detected in dodecane, cumene, or dodecane-15% cumene. However, gum was detected in dodecane and dodecane-15% cumene doped with thiols and disulfides. Alkyl thiols and disulfides reduced the rate of autoxidation of dodecane, and there was an induction period in the formation of gum. Traces of sulfur (=4 ppm) inhibited the autoxidation of dodecane-15% cumene in a way that resembled the post autoxidation of Jet A. Adding an organic base increased the rate of post autoxidation in Jet A and prevented formation of the oxidation inhibitor. An inhibition mechanism is proposed in which phenols are formed via acid-catalyzed decomposition of benzylic hydro peroxides.

Nomenclature
C = Carbon
O = Oxygen
N = Nitrogen
S = Sulfur
R• = Free Radcal
Φ = an Alkyl or Phenyl Group
mL = milli-liter
µmoles = micro-moles
nm = nano-meters
FTIR = Fourier Transform Infrared
LIF = Laser Induced Fluorescence
GC= Gas Chromatography
TBDS = t-Butyl Disulfide
NBDS = n-Butyl Disulfide
PDS = Phenyl Disulfide

INTRODUCTION

With advances in jet engine technology and the quest to reach higher mach numbers, the thermal stability of jet fuel has become paramount in the thermal management of modern aircraft (Edwards, et al., 1992). Higher fuel-system temperatures increase the rate of gum and deposit formation, which lowers heat-exchanger efficiency, plugs filters, and disrupts flow patterns in fuel nozzles. Deposits and gums result from autoxidation, which produces hydro peroxides and various oxygenates. Some of the oxygenates polymerize, and in that process, combine with sulfur and nitrogen compounds in the fuel to form gums. Deposits and gums are rich in oxygen and contain much higher concentrations of sulfur and nitrogen than the fuel (Peat, 1992).

Mayo, et.al., 1986 conclude that deposition is preceded by gum formation. Since gums form via fuel autoxidation, deposition should increase in direct proportion to the rate of autoxidation. To the contrary, an anomalous relationship exists between the rate of autoxidation and the rate of deposition (Heneghan and Zabamick, 1994, and Hardy, et al., 1991). Fuels that autoxidize with ease tend to form fewer deposits, or require higher temperatures to form deposits than fuels that have a resistance to autoxidation.

While the pathway to deposits seems to be linked to gums, the results of Hardy, et al., 1991 suggest that it includes something more than gum because the rate of gum formation is, for the most part, in direct proportion to the rate of autoxidation. The anomalous relationship between deposition and the rate of autoxidation suggests that there is another aspect of the mechanism that not only inhibits autoxidation, but also transforms gum into the relatively hard deposits that form in heat exchangers and fuel nozzles.

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To explain the oxidative resistance of jet fuels, which have a propensity to form deposits, Heneghan and Zabarnick, 1994, and Jones and Balster, 1997 proposed that naturally occurring antioxidants are responsible for both inhibiting autoxidation and forming deposit precursors. Mushrush, et al., 1996, and Zabarnick, 1998 concluded that sulfur compounds inhibit autoxidation by decomposing HPs into non-radical products, otherwise HPs enhance autoxidation via, ROOH = RO• + HO• (Fodor, et. al., 1988).

Taylor and Wallace, 1968 showed that sulfur compounds significantly enhanced the formation of deposits, while Mushrush, et al., 1996, and Kalitchin, et. al., 1992 found that they inhibited autoxidation and reduced the formation of insolubles.

The goal of the present study was to determine the mechanism of sulfur inhibition and the role it plays in the formation of deposits.

**EXPERIMENTAL**

Fuels were stressed in a reactor constructed from a 4-inch O.D x 5-inch solid aluminum cylinder. See Naegeli, et. al., 1997, 1998 for details. Ten ports machined symmetrically about the central axis of the cylinder housed glass ampules. A Chromelox cartridge heater placed along the central axis, and a thermocouple was inserted between two of the ampule ports in the reactor. Reactor temperature was maintained at 160±0.5°C by a Watlow series 965 controller.

Glass ampules (sealed volume 14.5 mL) from Fisher Scientific were filled with 5 mL of fuel. The fuel sample and the 9.5-mL head space were purged with pure oxygen prior to flame-sealing the ampule. The sealed ampules contained approximately 350 μmoles of oxygen.

The “kinetic clock” was started 7 minutes after the ampules were inserted into the reactor ports, i.e., the time required to heat the fuel to the 160°C isotherm. Ampules were removed from the reactor for analysis at times dependent on the projected rate of reaction.

**Analytical**

Stressed fuel samples were analyzed for HPs, soluble gum and oxygen remaining in the head space of the ampule. The techniques used are describe in Naegeli, et. al., 1997, 1998.

Oxygen consumption was determined by pressure change inside the ampule. It was assumed that the oxygen in the head space became fixed as liquid phase oxygenates, and that gaseous products such as CO2 and CH4 had negligible partial pressures.

Hydroperoxide was determined by the method of Egerton, et al., 1954 for aqueous HP. The spectrophotometric method was adapted to non-aqueous HPs using a reagent consisting of 1 mL of titanous chloride (19 wt.%) in 50 mL of concentrated hydrochloric acid and 150 mL of concentrated acetic acid. One mL of fuel was mixed with 5 mL of reagent and agitated for 30 seconds. The fuel and reagent were immiscible, so centrifuging was required to separate emulsified fuel from the reagent phase. HP was determined by measuring the optical density of the reagent phase at 428 nm with a Shimadzu UV-2101PC, visible-UV scanning spectrophotometer.

Calibration standards were prepared by dissolving cumene HP and t-butyl HP in Jet A and measuring the HP concentration by D 3703. Both standards gave the same response per mole of HP.

**RESULTS & DISCUSSION**

Concentration profiles over time of oxygen, HP, and gum were measured in clay-treated Jet A, dodecane, cumene, and a dodecane-15%-cumene blend at 433 K. Similar experiments were performed on dodecane and dodecane-15% cumene doped with sulfur compounds.

Figure 1 shows the concentration versus time profiles for clay-treated Jet A, dodecane, and dodecane-15% cumene. Gum is assumed to be proportional to LIF Intensity; HP is the μmoles formed in the 5 mL fuel sample, and oxygen is the
Table 1. Properties of Clay-Treated Jet A

<table>
<thead>
<tr>
<th>Property</th>
<th>Method</th>
<th>Meas.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density @ 15.5°C, g/cm³</td>
<td>D 4052</td>
<td>0.8164</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>D 93</td>
<td>59.0</td>
</tr>
<tr>
<td>Initial Boiling Point, °C</td>
<td>D 2887</td>
<td>121.0</td>
</tr>
<tr>
<td>10% off, °C</td>
<td></td>
<td>179.0</td>
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<tr>
<td>50% off, °C</td>
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<td>218.0</td>
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<td>90% off, °C</td>
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<td>256.3</td>
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<td>Final Boiling Point, °C</td>
<td></td>
<td>285.9</td>
</tr>
<tr>
<td>Sulfur, ppm</td>
<td>D 5453</td>
<td>262</td>
</tr>
<tr>
<td>Nitrogen, ppm</td>
<td>D 4629</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Paraffins, Vol.%</td>
<td>D 1319</td>
<td>82.0</td>
</tr>
<tr>
<td>Olefins, Vol.%</td>
<td>D 1319</td>
<td>2.0</td>
</tr>
<tr>
<td>Aromatics, Vol%</td>
<td>D 1319</td>
<td>16.0</td>
</tr>
<tr>
<td>Aromatics, wt%</td>
<td>D 5186</td>
<td>18.9</td>
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<tr>
<td>Mono-cyclic, wt%</td>
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<tr>
<td>Di-cyclic, wt%</td>
<td></td>
<td>3.2</td>
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<tr>
<td>Poly-cyclic, wt%</td>
<td></td>
<td>0.05</td>
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<tr>
<td>Existent Gum, mg/dL</td>
<td>D 381</td>
<td>0.0</td>
</tr>
<tr>
<td>JFTOT Break-Point, K</td>
<td>D 3241</td>
<td>590</td>
</tr>
</tbody>
</table>

The figure shows rapid autoxidation of dodecane and dodecane-15% cumene, but no LIF evidence of gum formation. For Jet A there is an induction period, over which there is neither gum nor peroxide formed, and very little oxygen consumed.

Analysis of a methanol extract of the Jet A, using the RULER (Kauffman, 1991) electrochemical method, indicated a phenolic-type antioxidant. The methanol-extracted Jet A had a much shorter induction period, suggesting that a good share of the antioxidant had been removed. Phenols cause induction periods in the autoxidation of jet fuels (Fodor, et al., 1992), and it is not uncommon to find them occurring naturally.

The induction period is followed by a relatively slow post autoxidation in which there is little oxygen consumption and HP build up. Initially, a small amount of oxygen is consumed relatively fast, but then the rate decreases to a near stand still. This behavior suggests that once the post autoxidation begins an inhibitor is produced that slows the autoxidation rate.

While the autoxidation almost stops, gum continues to form and does not seem to be strongly dependent on the rate of autoxidation. The precursors to gum seem to form quickly at the start of the post autoxidation. Since sulfur was present in Jet A and not in dodecane or cumene, it was suspected of causing both gum formation and inhibition of the post autoxidation. As will be shown later, this was investigated by examining the effects of sulfur compounds on the autoxidation of dodecane and dodecane-15% cumene.

Figure 2 shows that cumene autoxidizes faster than dodecane and forms much higher concentrations of HP. This was expected since the order of free-radical stability or abstraction of H from a C-H bond is benzylic H > tertiary H > secondary H > primary H (Walling, 1957). In other words, alkyl C-H groups adjacent to the aromatic ring are most reactive. While cumene HP forms faster than dodecane HP, it also appears to be more stable. This suggests that cumene is responsible for most of the HP buildup in the dodecane-15%-cumene blend.

To better understand the autoxidation of dodecane, the oxygenates formed were examined with FTIR and GC. Spectra were obtained by subtracting the spectra of the neat and stressed dodecane samples. Three relatively strong bands at 1419.4, 1575.6, and 1716.3 cm⁻¹ indicated that a β-diketone was the predominant product in stressed dodecane. GC analysis using a boiling point column (D 2887 method) showed a strong peak in the C₉₅ boiling point range, which accounted for about 70% of the oxidation products in stressed dodecane.

The β-diketone is of interest because the enol form is more stable than the keto form. Because of its vinyl structure,
the enol form could be induced to polymerize by a free-radical mechanism. A soluble gum was produced by stressing dodecane in an oxygen atmosphere for several hours at 433 K. The gum, which was soluble, was isolated by air-jet evaporation and analyzed for carbon and hydrogen. It appeared to be a dimer of the β-diketone, because its carbon and hydrogen contents were consistent with the empirical formula, C_{12}H_{22}O_2, and its average boiling point was similar to a C_{n} alkane.

Mayo, et al., 1982, 1986 also found a soluble gum in stressed dodecane and detected autoxidation products with molecular weights similar to the β-diketone and the dimer observed in the present study.

Hazlett, et al., 1977, and Reddy, et al., 1988 performed autoxidation experiments on dodecane in a JFTOT. The products consisted of alkanes and alkenes lighter than dodecane, C_{12} - alcohols, ketones, HP, and a cyclic ether. They attributed the light hydrocarbons to surface cracking, the alcohols and ketones to HP decomposition, and the cyclic ether to a sequence of reactions involving isomerization of the dodecyl hydroperoxy radical. A similar sequence of isomerization reactions may be envisioned to explain the formation of the β-diketone proposed in the present study.

**Dodecane + Sulfur**

Among the sulfur compounds investigated, SO_{2} was of particular interest because it was formed copiously in the autoxidations of cumene and tetralin doped with sulfur compounds (Holdsworth, et al., 1964). Furthermore, Naegeli and Marbach, 1988 observed increased deposition in fuels and lubricants doped with SO_{2} using a JFTOT.

There was no change in the autoxidation of dodecane when dodecane was doped with 50 ppm of sulfur as SO_{2}. The concentration vs. time profiles were the same as those in Figure 1. However, when SO_{2} was added to stressed dodecane, a gum-like substance began to form at room temperature. In less than an hour, a strong LIF signal developed and a black insoluble gum formed when the mixture was heated. It was clear that SO_{2} reacted with the autoxidation products of dodecane. Since no gum formed during the autoxidation of dodecane doped with SO_{2}, it was concluded that the SO_{2} oxidized to sulfuric acid before significant oxygenates were formed.

To explain the results, it is proposed that a 6-diketone “vinyl form” in stressed dodecane reacts with SO_{2} to produce a polyolefin-sulfone. According to Gritter, et al., 1978, and Bowden, et al., 1982, polyolefin-sulfones tend to decompose reversibly back to the olefin and SO_{2} above 473 K, therefore they could account for insolubles formed at lower temperatures, but they may not fully explain higher-temperature deposition in heat exchangers and fuel nozzles.

Figures 3 and 4 show the effects of doping dodecane with thiols and disulfides, respectively. Thiols and disulfides caused induction periods in both the oxygen disappearance and gum formation, but did not cause the same type of inhibition that was observed in the post autoxidation of Jet A.

Figure 3 shows that BT and HT cause induction periods in the autoxidation and formation of gum. BT causes a longer induction period than HT at the 50-ppm sulfur level. Mushrush, et al., 1996, explain the antioxidant character of thiols by the reaction sequence,

\[ \Phi-SH + R \rightarrow \Phi-S + RH \]
\[ \Phi-S + \Phi-S \rightarrow \Phi-S-S-\Phi \]

where free radicals abstract H atoms leaving thionyl radicals, which recombine to form the disulfide. The mechanism is similar to what happens in the oxidative conversion of thiols to disulfides in fuel sweetening processes.

Figure 4 shows that PDS has no effect on the rate of autoxidation. For NBDS, the inhibiting effect is slight at the 50-ppm sulfur level, but it becomes quite pronounced at the 100- and 200-ppm sulfur levels. The higher concentrations of HT and NBDS decreased the rate of autoxidation and reduced the rate of gum formation. NBDS and HT do not cause an induction period typical of most antioxidants. They just retard the rate instead of completely stalling the autoxidation.

After the induction periods shown in Figure 3, gum formed faster in dodecane doped with 50 ppm of sulfur as HT than in dodecane doped with 50 ppm of sulfur as BT. In a similar way, Figure 4 shows that gum formed faster in dodecane doped with 50 ppm of sulfur as NBDS than in dodecane doped with 50-ppm sulfur as PDS. These results show that alkyl thiols and disulfides form gum more rapidly than the aromatic derivatives.
The thiols and disulfides caused significantly longer induction periods for gum formation than for oxygen disappearance and HP formation. Except for BT, there was no induction period for HP formation in dodecane doped with thiols and disulfides at the 50-ppm sulfur level. In other words, the HP profiles in Figures 3 and 4 give little support of the theory that sulfur compounds act as HP decomposers.

To account for the relatively long induction periods for gum formation, it is concluded that thiols and disulfides have to oxidize before gum can form. Mushrush, et al., 1996 found that disulfides oxidize to disulfones. Since "alkyl" thiols and disulfides cause the gum to form faster than "aromatic" thiols and disulfides, it is proposed that they produce SO₂ via

\[ \Phi-\text{CH}_2\text{CH}_2\text{SO}_2\text{SO}_2\text{-CH}_2\text{CH}_2\Phi \rightarrow 2\cdot\text{CH}_2\text{CH}_2\cdot\text{SO}_2^\cdot \]

\[ \Phi-\text{CH}_2\text{CH}_2\text{SO}_2^\cdot + \text{R}^+ \rightarrow \Phi-\text{CH}=\text{CH}_2 + \text{SO}_2 + \text{RH} \]

In this reaction sequence, the disulfone decomposes to sulfonyl radicals, which react with chain-carrying radicals at the beta-carbon position to form an olefin, SO₂, and RH. Since the second reaction in the sequence consumes radicals used in chain propagation, it retards autoxidation. A similar reaction involving an aromatic disulfide is not possible so there would not be an inhibiting effect. For example, the benzene sulfonyl radical would have to decompose to form SO₂. Such a reaction would have a much higher activation energy than the radical abstraction reaction.

If SO₂ reacts with autoxidation products to form polyolefin-sulfones, it is a key precursor to gum. Since water is a product of autoxidation, SO₂ may also oxidize and form sulfuric acid.

**Dodecane-15% Cumene + Sulfur**

Figure 5 shows the effects of SO₂ and TBDS on the autoxidation of the dodecane-15%-cumene blend. Both SO₂ and TBDS strongly inhibit the autoxidation of dodecane-15% cumene. Autoxidation essentially ceases with as little as 4-ppm sulfur as SO₂. Over 300-ppm sulfur as TBDS is required to equal the effect of SO₂.

Gum is formed in dodecane-15% cumene doped with 20- and 50-ppm sulfur as TBDS, while almost none is formed at the 8- and 300-ppm sulfur levels. With 300 ppm there appears to be too little autoxidation, and with 8 ppm there is too little SO₂ to make gum.

Inhibition is also evident from the decrease in HP levels as the TBDS concentration is increased. Almost no HP is formed when dodecane-15% cumene is doped with just 4 ppm sulfur as TBDS.
ppm of sulfur as SO₂.

Figure 6 shows the effects of TBDS, TDT, TA, and PDS on the autoxidation of the dodecane-15%-cumene blend. Gum is not formed with the sulfide, TA, but it is formed by the disulfides, TBDS and PDS, and the thiol, TDT. The aromatic disulfide, PDS, forms more gum than the alkyl disulfide, TBDS, because it has no inhibiting effect on the autoxidation. The alkyl disulfide, TBDS, and thiol, TDT, strongly inhibit autoxidation in a way that resembles the inhibition in the post autoxidation of Jet A in Figure 1.

The gum formed with TBDS, TDT, and PDS has an induction period of about 30 minutes, but there is no induction period in the disappearance of oxygen. This supports the theory that sulfur compounds have to oxidize and probably form SO₂ before gum can form.

It is not clear why HPs are higher than baseline in dodecane-15% cumene doped with TA and PDS. It is contrary to studies of Mushrush, et al., 1996, Jones and Balster, 1997, and Zabamick, 1998, which claim that sulfur compounds are HP decomposers. On the other hand, it seems reasonable that TBDS and TDT suppress HPs because they strongly inhibit autoxidation.

Doping dodecane-15% cumene with other sulfides such as hexyl sulfide, phenyl sulfide, and thiophene gave the same result as doping with TA, i.e., there was no inhibiting effect on the autoxidation and no gum formation.

Inhibition Mechanism

The results show that as little as 4 ppm of sulfur in the form of SO₂ strongly inhibits the autoxidation of dodecane-15% cumene, whereas SO₂ has no effect on the autoxidation of dodecane. Thiols and disulfides cause inhibition in dodecane, but not at all like that observed in dodecane-15% cumene. Inhibition in dodecane-15% cumene is similar to that in Jet A in that it does not become pronounced until a small amount of oxygen is consumed. This suggests that oxidation of the sulfur compound causes an inhibitor to be formed.

Kauffman, 1995 detected phenols in thermally stressed Jet A doped with sulfur compounds. Phenols were not found in a stressed Jet A that had been hydrotreated to remove sulfur.

Holdsworth, et al., 1964 investigated the effect of sulfur compounds on the autoxidation of tetralin and the decomposition of cumene HP and tetralin HP. They found that sulfur compounds decomposed cumene HP into phenol
and acetone. Tetralin HP decomposed into 1-tetralone, 1,2-dihydro naphtalene and 1,2-dihydro naphthalene and 1-hydroxy-phenylbutyraldehyde, which is a phenol. However, in the process of decomposing HPs, copious amounts of SO₂ were formed. They concluded that SO₂ catalyzed the decomposition of HPs and proposed a cationic mechanism.

Actually, the decomposition of benzylic HPs to phenols is acid catalyzed. The classic example (Morrison and Boyd, 1966) is the acid catalyzed decomposition of cumene HP to phenol and acetone via

\[ \Phi-\text{C(CH}_3\text{)}_3\text{OOH} + \text{H}_2\text{O}^+ \rightarrow \Phi-\text{OH} + (\text{CH}_3\text{)}_3\text{CO} + \text{H}_2\text{O}^+ \]

where \( \Phi \) is a phenyl group. In this regard, sulfuric acid formed by oxidizing SO₂ is a potent catalyst. Since phenols make excellent oxidation inhibitors (Fodor, et al., 1992) their formation explains the inhibited autoxidation observed in dodecane-15% cumene and Jet A. Jet fuels contain alkyl substituted aromatics that autoxidize to benzylic HPs.

Jet A was doped with TDA to test if an acid was responsible for the formation of the oxidation inhibitor. Being that TDA is a weak base, it was used to neutralize any acid that might form during autoxidation.

Figure 7 shows that TDA greatly increases the rate of autoxidation and the formation of HP and gum. TDA has no effect on the induction period for autoxidation, but it delays gum formation. Note that gum is expected to form soon after oxygen begins to disappear. The results suggest that TDA not only neutralizes acid, but may also tie up a key reactant, e.g., SO₂, in the gum-forming process. The results are consistent with the theory that an acid catalyzes the cationic decomposition of benzylic HPs to phenols.

One possible explanation of the anomalous relationship between deposit formation and the rate of autoxidation is that phenols not only act as oxidation inhibitors, but also play a role in converting soluble gums to more stable high-temperature deposits.

Phenols appear to be involved in the formation of deposits. Hazlett & Power, 1983, found increased insolubles formed in thermally stressed fuels when a phenolic extract was added. Infrared spectra indicated that oxidative coupling (White, et al., 1983) of the phenols was responsible for the increased instability of the fuel.

Phenols may also react with aldehydes to form Bakelite (Morrison and Boyd, 1966). The analogous reaction with ketones is thought to be relatively slow, but at high temperatures phenols might form Bakelite-like linkages with the ketone groups in soluble gums. In other words, phenols could link gums together to create a more stable, higher-molecular-weight deposit.

CONCLUSIONS

The conclusion of this study is that sulfur in jet fuels causes the formation of oxidation inhibitors, which may play a role in the formation of deposits at high temperatures. The oxidation inhibitors are phenols formed by the acid-catalyzed decomposition of benzylic HPs. Adding an organic base neutralizes the acid and increases the rate of autoxidation in Jet A. It is concluded that neutralizing the acid prevents formation of the oxidation inhibitor.

Relatively low concentrations of alkyl thiols and disulfides strongly inhibit the autoxidation of dodecane-15% cumene in a way that resembles the inhibition in Jet A. The inhibiting effect is much stronger when the blend is doped with SO₂. During the autoxidation, thiols and disulfides oxidize to form key intermediates, such as SO₃, that react to form gum. SO₂ also oxidizes to sulfuric acid, which catalyzes decomposition of benzylic HPs.

Alkyl thiols and disulfides form reactive intermediates such as SO₃ much faster than their aromatic derivatives. The rate of autoxidation of dodecane is less sensitive to thiols and disulfides than that of dodecane-15% cumene. In dodecane, alkyl disulfides appear to inhibit autoxidation by forming sulfonyl radicals, which react with chain-carrying radicals to form non-radical products. Organic sulfides do not cause gum formation nor do they change the rate of autoxidation of dodecane and dodecane-15% cumene.

This study concludes that disulfides are especially important in fuel stability, because they are often present in fuels as the result of sweetening. The sweetening process used in fuel refinement converts thiols to disulfides, which

![Figure 7. The Effect of TDA on the Autoxidation of Jet A](image-url)
according to this study does little to improve fuel stability.

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