

PYROLYTIC DEGRADATION OF COAL- AND PETROLEUM-DERIVED AVIATION JET FUELS AND MIDDLE DISTILLATES

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INTRODUCTION

The thermal stability of jet fuels plays an important role in the design and development of future hypersonic aircraft. It was reported that the fuel in these new hypersonic aircraft may reach temperatures higher than 500°C. The temperatures are much higher than the current maximum operating temperature for the conventional aviation jet fuels. When the fuels are exposed to such high temperatures, serious pyrolytic degradation of the fuels will occur and will result in the formation of solid deposits on critical aircraft systems such as fuel pipeline, filter, and engine parts (Roquermore et al., 1989). This means that advanced jet fuels are required for hypersonic aircraft. The development of such fuels warrants detailed study of pyrolytic degradation of hydrocarbon fuels.

The ultimate goal of our research project is to develop advanced jet fuels that are thermally stable at high temperatures. The objectives of this work are to rank the thermal stability of current fuels, to identify thermally stable compounds in fuels, to clarify the chemistry of pyrolytic degradation and mechanisms of solid formation, and to enhance the intrinsic stability of jet fuels by optimizing fuel composition. The future fuels might derive not only from petroleum, but also from hydrocarbon resources such as coal, tar sands, and oil shale. The scope of this paper will concentrate on the thermal stability study of ten fuels including four coal-derived fuels and six petroleum-derived military and commercial jet fuels. The results concerning the effects of hydrogen-donors on the fuel stability are presented in Song et al. (1992b). In this study, the relative thermal stabilities of the fuels have been elucidated by their chemical composition.

EXPERIMENTAL

Apparatus and Procedures

Thermal stressing of the jet fuels and middle distillates were studied in tubing bomb reactors at 450°C for a heating period of 0-8 hours under 0.69 MPa UHP-N₂. The tubing bomb reactors were described in detail elsewhere (Eser et al., 1990). A 5 ml sample was confined in a leak-tested reactor. The sample was deoxygenated through repetitive (6 times) pressurization to 6.9 MPa with UHP-N₂ and purging to remove oxygen/air in the reactor or dissolved in the sample. The reactor was pressurized to the desired starting pressure of 0.69 MPa with UHP-N₂ before being immersed into a fluidized sand bath which has been preheated to 450°C. After the experiment was started, the reaction pressure was closely monitored. The experiment was ended after the desired stressing time by removing the reactor from the fluidized sand bath and immediately quenching in a cool water bath. The headspace gas was collected in a gas sampling bag.

Product Chemical Analysis

The gas samples were analyzed for their compositions and quantities by using a Perkin-Elmer Autosystem gas chromatograph (GC). Two detectors, a thermal conductivity detector (TCD) and a flame ionization detector (FID), were used to analyze the gas composition. The TCD was used to determine CH₄, C₂H₂, C₂H₄, and C₂H₆ as well as non-hydrocarbon gases such as H₂, CO, and CO₂. The FID was used to detect hydrocarbon gases from C₁ to C₆. The GC columns used were a 10 feet long, 1/8 inch diameter stainless steel column packed with 100/120 Carbosieve SII (Supelco) for TCD and a 6 feet long, 1/8 inch diameter stainless steel column packed with 80/100 Chemipack C 18 for FID. There are two liquid samples collected from each experiment: one is the liquid residue directly collected

from the reactor and the other is washed from the reactor wall with pentane. The compounds in the liquid products were identified by a HP 5890 Series II GC coupled with HP 5971A Mass Selective Detector (MSD) and quantified by a Perkin-Elmer GC 8500. The column used was a 30 m, 0.25 mm i.d., DB-17 Fused Silica Capillary Column (50% phenyl, 50% methyl silicone) with a film thickness of 0.25 μm . The solid deposits are operationally defined as the materials which are not soluble in the resulting liquid co-products and pentane (washing solvent). The solid deposits are to be analyzed by Fourier transform infra-red spectroscopy and NMR spectroscopy.

Samples

Ten jet fuels and middle distillates were studied. Four coal-derived fuels include JP-8C from hydrotreating of liquids produced from the Great Plains Gasification plant, and middle distillates derived either from direct coal liquefaction (WI-MD from Wilsonville plant and HRI-MD from HRI) or from indirect coal liquefaction (FT-MD from Fischer-Tropsch synthesis). Six petroleum-derived military and commercial jet fuels include JPTS (thermally stable jet fuel), JP7, JP-8P, JP-8P2, Jet A, and Jet A-1. The basic information of these fuels is presented in Table 1, and the properties of the samples are discussed in the following section.

RESULTS AND DISCUSSION

Properties of Samples

The fuel densities range from 0.76 g/cm^3 (FT-MD) to 0.96 g/cm^3 (WI-MD) with most falling in a smaller range of 0.79 to 0.81 g/cm^3 (JPTS, JP-7, JP-8P, Jet A, Jet A-1, and JP-8P2). The densities of JP-8C and HRI-MD are 0.84 and 0.92 g/cm^3 , respectively. All the fuels were analyzed by GC and GC-MS before and after thermal stressing, and they are all complex mixtures of hundreds of compounds. Because of the large number of compounds in the fuels, one way to visualize their compositions is employing the total ion chromatograms (TIC) and specific ion chromatograms (SIC) of GC-MS analysis. Figure 1 presents the TIC and SIC (ions of m/z 57, 83, 91, 105, and 142) of JP-8P2. The fragment ions of m/z 57, 83, and 142 are characteristics of long-chain paraffins, alkylcyclohexanes, and alkylnaphthalenes, respectively. The ions of 91 and 105 imply the presence of alkylbenzenes. From the resemblance between TIC and SIC of m/z 57, we can find that the dominant constituents in JP-8P2 are the long-chain paraffins with carbon-number ranging from C_8 to C_{17} with most falling between C_{10} to C_{15} . The alkylbenzenes (C_2 - C_6 -, mainly C_3 - C_5 -) content is about 20 percent. JP-8P2 also includes 5% alkylcyclohexanes (C_3 - C_8 -) and low concentrations of tetralin, alkyindan, and alkylnaphthalenes.

JP-8P, Jet A, JP-7, FT-MD, JPTS, and Jet A-1 are also paraffinic fuels derived from petroleum with long-chain paraffins as the dominant constituents, but the overall compositions and paraffins distributions are somewhat different. Figure 2 shows the SIC (m/z 57) for six of the seven paraffinic fuels. We can see that JP-8P and Jet A are quite similar to JP-8P2 in terms of the long-chain paraffins distributions. Jet A-1 has a narrower band from C_{10} to C_{14} with most falling between C_{11} and C_{12} . JPTS has a band from C_9 to C_{15} . JP-7 has a band from C_{11} to C_{16} with an average carbon number of 12. FT-MD is also a paraffinic fuel, although derived from coal, having almost exclusively paraffins (C_9 - C_{21}) with very low concentration of cycloparaffins. Table 2 summarizes the approximate compositions of the seven paraffinic fuels based on the three major hydrocarbon types found in fuels (paraffins, alkylbenzenes, alkylcyclohexanes) and others (such as alkylnaphthalenes, alkyindans, etc).

JP-8C, WI-MD, and HRI-MD are all coal-derived fuels, but their compositions are quite different from petroleum-derived paraffinic fuels. JP-8C is composed mainly of monocyclic and bicyclic alkanes, and two-ring hydroaromatic compounds. The major components are alkyl-substituted cyclohexanes (about 45%), decalin (6.3%), C_1 -decalin (4%), and tetralin (3.9%). There are also about 10% alkylbenzenes. HRI-MD is a heavy fuel, i.e., with many high molecular-weight components compared with the paraffinic fuels and JP-8C. HRI-MD consists of (alkyl) bicyclic alkanes, alkyl two-ring aromatic compounds and some alkylbenzenes. There are about 15% alkyl-substituted (mainly, C_0 - C_3 -) cyclohexanes and only 8% long-chain paraffins. There are also some (C_0 - C_2 -) 3-ring or 4-ring aromatics. Regarding WI-MD, it is heavier (with carbon number ≥ 12) than the other nine fuels with few light molecular weight compounds. It has very high content of aromatics (with ring size not less than 2). The most abundant peaks are pyrene (4%) and multi-hydropyrenes (total about 8%), and less than 10% paraffins (C_{14} - C_{25}).

Degradation Product Distributions and Stability Comparison

The relative thermal stabilities of hydrocarbons in fuels as well as the whole fuels themselves were identified based on the overall reaction products (gas, liquid, and solid) distributions and GC/GC-MS analysis of the liquid products. For the hydrocarbons in fuels, it was found that at 450°C long-chain *n*- and iso-paraffins ($\geq C_{11}$), and *n*-alkylbenzenes (alkyl $\geq C_3$ -) are some of the unstable compounds. Some compounds that are relatively more stable compounds include long-chain paraffins ($\leq C_8$), long-chain paraffins (C_9 and C_{10} , up to 4 hr), C_0 - to C_3 -cycloalkanes, and C_0 - to C_2 -benzenes. One example is shown in Figure 3, which presents the total ion chromatograms of the neat sample of, and the liquid products from, FT-MD after thermal stressing at 450°C for 1-8 hours. Recall that FT-MD is a paraffinic fuel which has paraffins ranging from C_9 to C_{21} . We can clearly find that long-chain paraffins of C_{11} through C_{21} decompose quickly; the decomposition rate increases with increasing chain size. Quantitative results from GC and qualitative results from GC-MS indicate that the main reactions occurring in the first 2.5 hours include cracking of the paraffins into lower alkanes and olefins, and cyclization to form alkylicyclic alkanes and olefins. The alkylicyclic compounds were then subjected to dehydrogenation to form alkylbenzenes. This observation is consistent with the mechanisms proposed by Song et al. (1992a). A quantitative presentation of how the paraffins content changes with time is shown in Figure 4 for the same sample. The paraffins were divided into 12 groups based on the carbon numbers; each group consists of straight and branched alkanes with the same carbon number. Figure 4 shows that at 450°C long-chain paraffins with carbon number no less than 11 (i.e., C_n , $n \geq 11$) are unstable. C_{15} through C_{21} decompose completely by 2.5 hours. Notice that the content of C_9 increases from the initial 0.5% to 5.7% at 1 hour and then decreases to 3.1% after 2.5 hours. The initial increase is contributed from cracking yield from longer chain paraffins, and the C_9 later decomposes and results in the C_9 fraction decreasing with increasing time.

The yields of the gas components from JP-8P thermally stressed at 450°C for 1-8 hours are presented in Figure 5. Methane is always the most abundant gaseous product (in mmole) followed by ethane and propane over the stressing range; this is also true for all other nine fuels studied. Another common characteristic for the fuels is that the paraffinic gases (CH_4 , C_2H_6 , C_3H_8 , and C_4H_{10}) increase with increasing time but the olefinic gases (C_2H_4 , C_3H_6 , C_4H_8) increase initially then decrease with increasing time. Continuous cracking accounts for the progressive increase of paraffinic gases and the initial increase of olefinic gases. Olefins are known to be less stable and highly reactive because of unsaturation; this results in the later decrease of olefinic gases.

The decomposition extents of the ten fuels are significantly affected by their compositions. Figure 6 shows the gas yields from the ten fuels stressed for 1-8 hours. The figure indicates that the three coal-derived non-paraffinic fuels, i.e., JP-8C, HRI-MD, and WI-MD, are more stable than the other seven paraffinic fuels in terms of less gas formation. The difference in stability in terms of the gas formation is attributed to the composition difference. Paraffinic fuels produce more gases because the major reaction for long-chain paraffins is cracking into lighter gases of alkanes and olefins. On the other hand, the compositions of the three coal-derived non-paraffinic fuels are quite different from the paraffinic fuels; they have low fraction of paraffins but are rich in cyclic alkanes and hydroaromatics. Thus the major reaction for them is dehydrogenation to form alkylbenzenes (liquid yields) instead of the formation of low molecular-weight gases. It can be seen that HRI-MD and FT-MD produce the gas the least and the most, respectively. For example, the gas yields for HRI-MD and FT-MD are respectively 3.3% and 17% at 1 hour, 10% and 33% at 4 hours, and 16% and 52% at 8 hours. The six petroleum-derived paraffinic fuels (JP-8P, Jet A, JP-7, FT-MD, JPTS, and Jet A-1) have similar gas yields (ranging from 37% to 40%) for 8-hour stressing. However, for 1- to 4-hour stressing, Jet A-1 has the lowest or second to the lowest gas yields; this is consistent with the fact that among the paraffinic fuels, Jet A-1 has the lowest paraffin content and the narrowest paraffin band (from C_{10} to C_{14} , with most falling between C_{11} and C_{12}).

The solid yields from the ten fuels stressed for 1-8 hours are presented in Figure 7. The figure shows that there is no solid formed after 1-hour stressing for all the ten fuels, and the solid starts to form between 1 and 2.5 hours. The induction time, which is the time period needed for the formation of solid precursors (such as polyaromatics) from reactive intermediates, differs for each fuel. It was found that fuels rich in hydrogen-donors (such as cyclic alkanes) have longer induction period and tend to have better stability. The hydrogen abstracted from hydrogen-donors stabilizes the reactive radicals; this in consequence inhibits the secondary radical reactions and suppresses solid formation (Song et al., 1992b). Two of the three coal-derived non-paraffinic fuels, JP-8C and HRI-MD, have much better stability than other fuels in terms of much less solid formation. This is again attributed to the composition

difference and the fact that JP-8C and HRI-MD have high concentration of hydrogen donors. Figure 7 also shows that JP-7 and JP-TS have higher stability among the seven paraffinic fuels in terms of less solid formation. This is also attributed to their lower aromatics content and higher hydrogen-donor compounds (alkylcyclohexanes).

WI-MD, on the other hand, does not have good stability in the long run, judging from its high solid formation at 8-hour stressing. Figure 8 presents the total ion chromatograms of the neat sample of, and the liquid products from, WI-MD after thermal stressing at 450°C for 1-8 hours. It can be seen that WI-MD has very high content of aromatics and hydroaromatics. The hydroaromatics decomposed quickly to form saturated aromatics through dehydrogenation, and these aromatic compounds subsequently form more polycyclic aromatic hydrocarbons and solid deposits. WI-MD seems to be stable in terms of low gas formation; however, GC-MS analysis of the liquid products shows that in fact WI-MD is quite unstable and decomposes quickly to form aromatics and precursors to solid. In short, WI-MD tends to form more solid than other fuels due to its high aromatic content nature, and it can not be a good jet fuel.

CONCLUSIONS

The thermal stability of the fuels is significantly affected by their chemical composition. Pyrolysis of ten jet fuels and middle distillates has been studied in a tubing bomb reactor. The compositions of the stressed as well as neat fuels were all qualitatively and quantitatively characterized by GC and GC-MS. This information is useful in explaining and evaluating the thermal stability of fuels. The relative thermal stabilities of hydrocarbons in fuels as well as the whole fuels themselves were identified. The fuels with higher contents of 1-3 ring cycloalkanes and/or hydroaromatics are more stable than those with higher contents of long-chain paraffins in terms of less gas formation. The former includes JP-8C, HRI-MD and WI-MD, and the latter covers the remaining 7 fuels including six petroleum-derived paraffinic fuels and one paraffinic fuel from indirect coal liquefaction. Among the paraffinic fuels, higher stability in terms of less gas formation was observed for those fuels having narrower distribution of paraffins with relatively shorter chain, e.g., Jet A-1; those with lower aromatics content and higher hydrogen-donor compounds exhibit less solid formation. Overall, coal-derived JP-8C and HRI-MD have the best thermal stability among the ten fuels studied either in terms of less gas or solid formation.

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Table 1. Coal- and Petroleum-Derived Jet Fuels and Middle Distillates

Fuel	Description	Received	Supplier/Source	Sample No.
Coal-Derived Fuels				
1) JP-8C	Hydrotreated JP-8	5-30-89	WPAFB	89-POSF-2685 ?
2) WI-MD	Middle distillates from coal liquefaction at Wilsonville	4-20-90	DOE PETC	259E MD
3) FT-MD	Middle distillates from Fischer-Tropsch Synthesis	8-16-91	DOE PETC	PETC F-T
4) HRI-MD	Middle distillates from coal liquefaction at HRI	11-26-91	WPAFB	83-POSF-0849
Petroleum-Derived Jet Fuels				
5) JP-8P	Petroleum-Derived JP-8	5-30-89	WPAFB	
6) JP-8P2	Petroleum-Derived JP-8	5-31-90	WPAFB/Tank S-15	
7) JP-7	Petroleum-Derived JP-7	5-31-90	WPAFB/Tank S-16	
8) Jet A-1	Commercial jet fuel	8-16-91	WPAFB/Tank S-7	90-POSF-2747
9) JPTS	Thermally stable jet fuel	8-16-91	WPAFB	91-POSF-2799
10) Jet A	Commercial jet fuel	8-16-91	WPAFB	90-POSF-2827

Table 2. Approximate Compositions of Paraffinic Fuels

Fuel	Weight %			
	Paraffins	Alkylbenzenes	Alkylcyclohexanes	Others
JP-8P2	~ 70%	~ 20% (C ₂ -~C ₆ -)	~ 5% (C ₃ -~C ₈ -)	
JP-8P	~ 75%	~ 12% (C ₂ -~C ₄ -)	~ 8% (C ₃ -~C ₇ -)	
Jet A	~ 80%	~ 10% (C ₂ -~C ₄ -)	~ 6% (C ₁ -~C ₆ -)	
JP-7	~ 90%	very low	~ 10% (C ₅ -~C ₈ -)	
FT-MD	~ 100%		low	
JPTS	~ 70%	~ 8% (C ₂ -~C ₄ -)	~ 13% (C ₁ -~C ₇ -)	
Jet A-1	~ 65%	~ 26% (C ₃ -~C ₅ -)	~ 6% (C ₄ -~C ₅ -)	

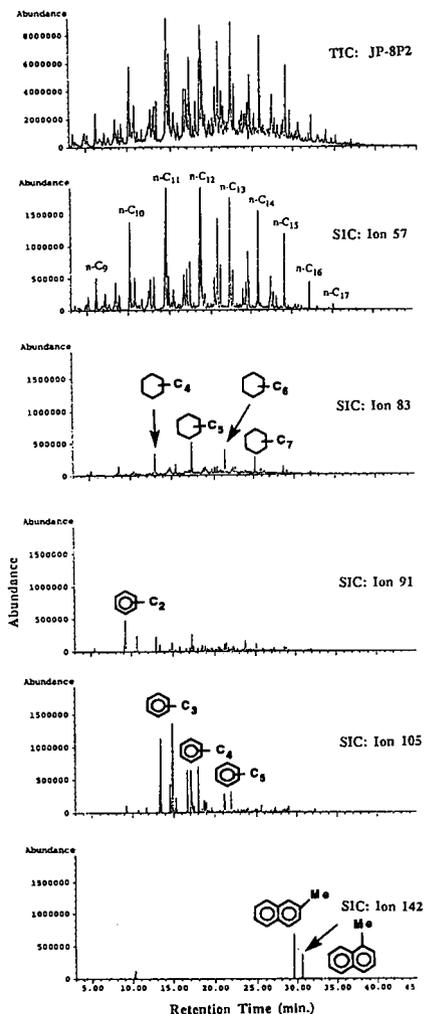


Figure 1. Total and specific ion chromatograms (ions of m/z 57, 83, 91, 105, and 142) of JP-8P2 from GC-MS analysis.

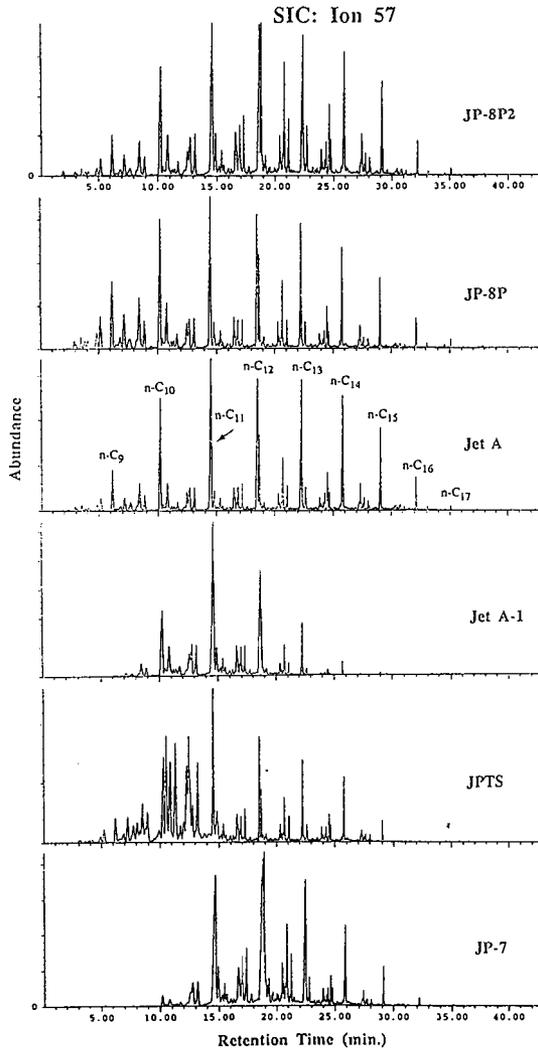


Figure 2. Specific ion chromatograms (ion of m/z 57) of six paraffinic fuels.

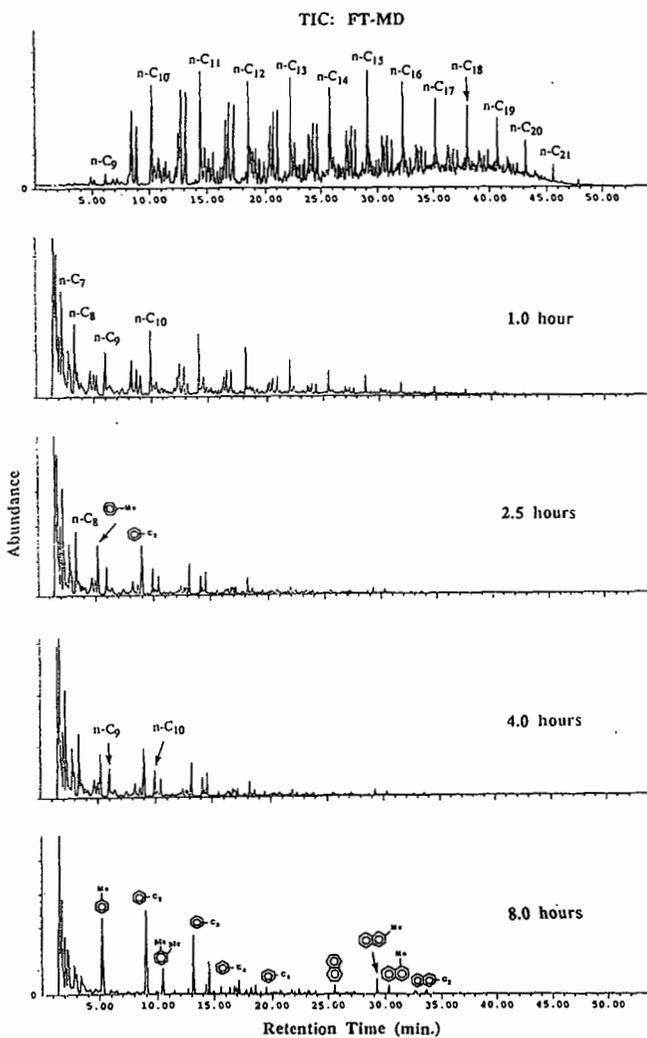


Figure 3. Total ion chromatograms of the neat sample of, and the liquid products from, FT-MD after thermal stressing at 450°C for 1-8 hours.

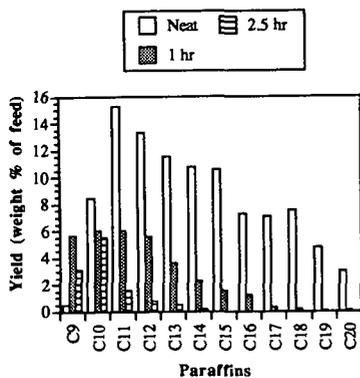


Figure 4. Paraffins distribution of liquids from FT-MD

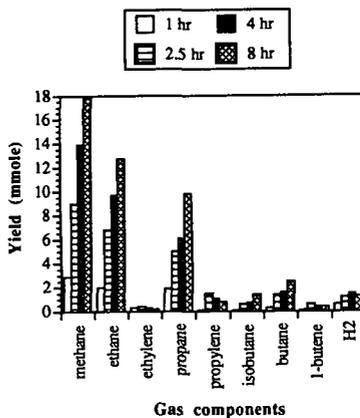


Figure 5. Yields of H₂ and C₁ ~ C₄ gases from JP-8P

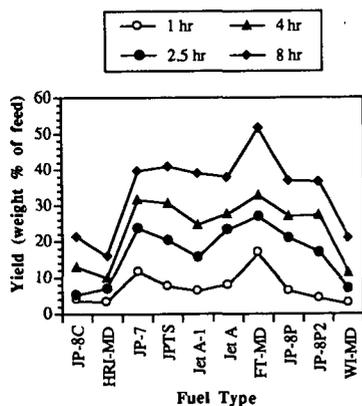


Figure 6. Yields of gases at 450°C

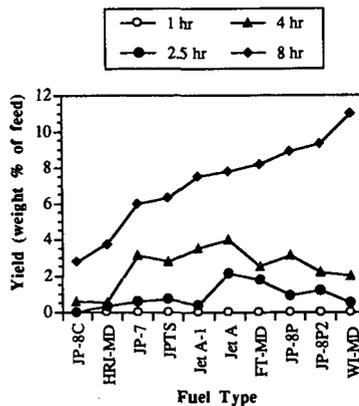


Figure 7. Yields of solid deposits at 450°C

