

Hydrogen-Transferring Pyrolysis of Cyclic and Straight-Chain Hydrocarbons. Enhancing High Temperature Thermal Stability of Aviation Jet Fuels by H-Donors

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INTRODUCTION

The present work is a fundamental study of condensed-phase pyrolysis of saturate hydrocarbons including alkylcyclohexanes, trans- and cis-steric isomers of decalin and straight-chain paraffins as well as hydroaromatics such as tetralin. This work is a part of an on-going research program for developing advanced jet fuels thermally stable at high temperatures. One of the critical problems in developing thermally stable jet fuels for high-Mach aircraft is the formation of solid from hydrocarbon fuels in pyrolytic regime (Roquemore et al., 1989; Hazlet, 1991). In studying the pyrolytic degradation of jet fuels, it occurred to us that hydrogen-transfer from H-donors, such as those present in coal-derived JP-8C jet fuel, could play an important role in suppressing thermal decomposition and solid formation (Song et al., 1991a, 1991b, 1992a, 1992b). The hydrogen-transferring pyrolysis described in this paper refers to the thermal decomposition of straight-chain and cyclic hydrocarbons in the presence of H-donors.

This paper reports on 1) pyrolytic degradation of the above-mentioned cyclic and straight-chain hydrocarbons; 2) inhibiting effects of H-donors on the decomposition and solid-forming tendency of n-tetradecane (n-C₁₄), n-butylcyclohexane (n-BCH), cis-decalin (cis-D) and n-butylbenzene (n-BB) as well as a petroleum-derived JP-8P jet fuel; and 3) the mechanisms of the pyrolysis and H-transferring pyrolysis. It should be noted that the experimental conditions used in this work are such that they are close to the high-temperature thermal environment of jet fuel in the future high-Mach aircraft under consideration. These conditions are characterized by condensed or supercritical phases, relatively high pressure, static reactor, and long residence time. Such conditions are distinctly different from those used in most previous paraffin pyrolysis work (vapor phase, low-pressure, flow reactor, short residence time).

EXPERIMENTAL

Reagent-grade n-C₁₄, n-BCH, ethylcyclohexane (ECH), trans-decalin (trans-D) and cis-decalin (cis-D), decalin, tetralin, n-butylbenzene (n-BB) from Aldrich and a petroleum-derived JP-8P jet fuel (Song et al., 1992a) were used. Several compounds including tetralin, decalin, cis-D and trans-D were also examined as H-donors. The pyrolysis was conducted at 450°C for 0-8 h under 0.69 MPa UHP-N₂ (cold) in 25 mL tubing bombs using 5 mL sample. A fluidized sandbath preheated to 450°C was used as heater. The products were identified by capillary GC-MS and quantified by GC. More experimental details may be found in a companion paper (Lai et al., 1992).

RESULTS AND DISCUSSION

I. Pyrolysis of Cyclic and Straight-Chain Hydrocarbons

We first conducted a comparative examination of thermal stability of several cyclic and straight-chain hydrocarbons, which are representative components in coal- and petroleum-derived jet fuels, respectively. Figure 1 shows the time-pressure profiles for the pyrolysis of these compounds. Since static reactor was used, the sample is always confined within the reactor. Therefore, the increase of system pressure after equilibrium boiling is indicative of the extent of thermal decomposition. As shown in Figure 1, when tetralin was heated under 0.69 MPa N₂ (cold) pressure, the system pressure increased to 3.4 MPa within 10 minutes, then the pressure maintained nearly constant. All the other compounds displayed more or less pressure increase. Their t-p profile patterns provide a convenient measure for the extent and rate of their thermal decomposition to form smaller molecules. It should also be noted from Figure 1 that the temperature of 450°C and pressures at 450°C (≥ 3.5 MPa) are higher than the critical temperatures and critical pressures of all the compounds, suggesting the occurrence of supercritical-phase pyrolysis.

Figure 2 shows the conversion of several compounds versus residence time at 450°C for 0-8 h. The typical component of petroleum jet fuels, n-C₁₄, exhibited the highest degree of decomposition, and its pyrolysis led to 50% conversion in just 30 min. For the cycloalkanes, the rate of n-BCH decomposition is faster than that of ECH, indicating that increasing the length of side chain on alkylcyclohexane decreases the thermal stability. Decalin appears to

be more stable than the other saturates (Eser et al., 1992, Song et al., 1992b) but it is originally a mixture of trans- and cis-D (see below). Tetralin was the most stable compound when stressed alone. Combination of the data in Figures 1 and 2 indicates that cycloalkanes are much more stable than the long-chain paraffins; the increase in the length of side-chain of alkylcycloalkanes or straight-chain paraffins decreases the stability and increases the decomposition rate.

Alkylcyclohexanes. Figure 3 shows the distribution of products from n-BCH as a function of conversion. At low conversion level of 11.8 mol%, the major products are cyclohexane (3.0, mol%), methylenecyclohexane (2.3), methylcyclohexane (1.9) and cyclohexene (1.1). Scheme I shows the possible reaction mechanisms proposed based on the identified products. The initiation reaction of n-butylcyclohexane is likely the homolytic cleavage of the C-C bond between the ring and the side-chain to form cyclohexyl and 1-butyl radicals. The formation of the four predominant initial products can be rationalized by the radical reaction pathways I, II, III, and IV, respectively. After 1 h at 450°C, the yield of methylenecyclohexane begins to decrease with further increasing residence time, presumably due to hydrogenation to form methylcyclohexane.

In regard to the reaction mechanisms for alkylcyclohexane pyrolysis, there is little information in the literature except for the recent report of Savage and Klein (1988), who found that there are only two major pathways for pyrolysis of n-tridecylcyclohexane. The pathways I and II for n-BCH are also consistent with their observations. However, the present work reveals that other major pathways, III and IV, also exist for the alkylcyclohexanes with shorter side-chains, as shown in Scheme I. Interestingly, when the residence time was extended to 2.5 h and longer, cyclohexane and methylcyclohexane become the two most predominant products, and their yields were several times higher than those of all the other products. These results suggest that pathways I and III dominate in long-duration n-BCH pyrolysis.

Scheme I. Possible Mechanisms for Pyrolysis of n-Butylcyclohexane

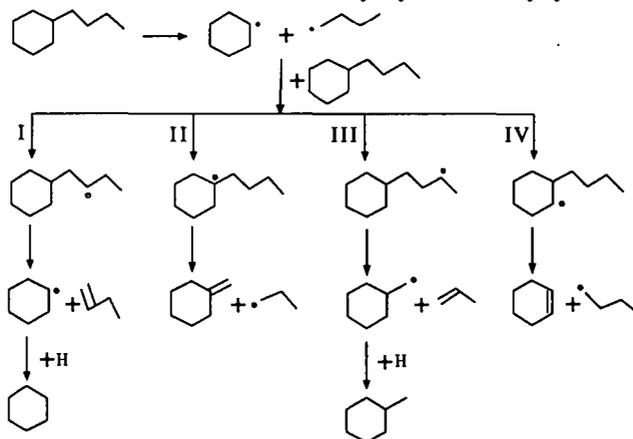
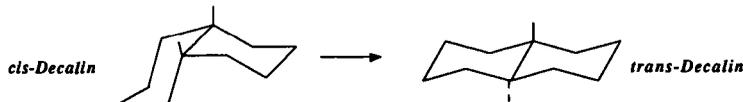


Figure 4 shows the distribution of products from ECH. At low conversion level (7.3 mol%), the major products from ECH are cyclohexene (1.50 mol%), methylcyclohexane (0.83 mol%), methylcyclohexene (0.87 mol%). The preference of cyclohexene formation indicates that the reaction via cyclohexyl radical is a major path, similar to path IV for n-BCH. However, methylenecyclohexane is a minor product in this case (0.17 mol%), indicating that one of the major pathways for n-BCH becomes a minor one for ECH. Another major difference between ECH and n-BCH is the higher yields of isomerization products from ECH pyrolysis, such as methylcyclopentane.

Decalin. Figure 5 shows the product distribution for pyrolysis of decalin, which was originally a mixture of nearly equivalent weights of trans- and cis-D. After decalin pyrolysis at 450°C, the yield of trans-D increased slightly and that of cis-D decreased monotonically with increasing time up to about 4 h. There are two possible reasons for such observations: isomerization of cis- to trans-D or decomposition of cis-D. To gain further insight, we performed the runs of pure trans-D and cis-D, as shown in Figure 6. It was found that cis-D is not stable and tends to isomerize into trans-D as outlined in Scheme II. Amount of trans-D formed from cis-D increased from 6% in 30 min to 41% after 4 h at 450°C. Roberts and Madison (1959) found that di-t-butylperoxide can initiate such an isomerization. Probably

this is initiated via H-abstraction by a radical from 9-position. On the other hand, trans-D is much more stable than cis-D. Its isomerization to cis-D also occurred but the extent was very limited, even after 8 h, as can be seen from Figure 6. In fact, trans-D was found to be one of the most stable components in coal-derived jet fuel JP-8C (Song et al., 1992a).

Scheme II. Isomerization of cis-Decalin to trans-Decalin

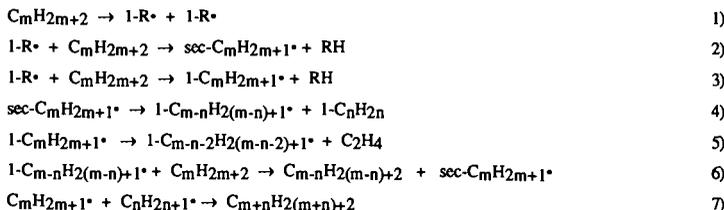


We also observed substantially higher gas yields from cis-D (5.4 wt% in 4 h) than from trans-D (0.8 wt% in 4h), showing higher degree of ring-opening cracking and subsequent dealkylation with cis-isomer. In the case of cis-D, 1-butylcyclohexene was also detected as a major cracking product (0.7 mol%) after 30 min at 450°C. It was formed probably via the 9-decyl radical and subsequent β -scission which caused the ring-opening cracking. The cracking via 9-decyl radical was also suggested for hydrolysis of decalin by Shabtai et al. (1979). Therefore, the ring-opening cracking and isomerization of cis-decalin may share the same initiation path, because the latter also involves 9-decyl radical formation as the first step. In summary, the steric conformation of cycloalkanes also affects their thermal stability, and for decalin, trans-isomer is much more stable.

n-Tetradecane Pyrolysis. Pyrolysis of n-tetradecane at 450°C for 0-8 h produced up to about 175 compounds, and the products ranged from lightest molecules such as hydrogen and methane to heavy polyaromatics such as pyrene and solid deposits. After 30 min at 450°C, 49% of n-C₁₄ has been decomposed, and the main products are C₁-C₁₃ alkanes and C₂-C₁₃ 1-alkenes. Scheme III shows the possible reaction pathways for thermal cracking of long-chain n-alkanes such as n-tetradecane under the conditions employed. The first substrate radicals from n-C₁₄ include both sec-C₁₄H₂₉[•] (eq. 2) and 1-C₁₄H₂₉[•] (eq. 3). Formation of the primary radical requires higher activation energy than that of secondary radical, but the difference is not very large in H-abstraction reaction. For example, the activation energies for H-abstraction from n-butane to form 2-C₄H₉[•] and 1-C₄H₉[•] at 427°C are 10.4 and 12.3 kcal/mol, respectively (Allara and Shaw, 1980).

There are two extremes of the same fundamental mechanism for radical reactions: the Rice-Kossiakoff mechanism and the Fabuss-Smith-Satterfield mechanism (Fabuss et al., 1966; Poutsuma, 1990), which afford different product spectra. Pyrolysis of long-chain paraffins is still the subject of many investigations. Several recent papers reported the preferential formation of 1-alkenes from vapor-phase pyrolysis of long-chain paraffins (Zhou et al., 1987; Fairburn et al., 1990). In the present work, significant amounts of olefins, mainly 1-alkenes, were also detected, both in liquid and gaseous products. However, unlike the literature results for high temperature and short-residence time pyrolysis, the olefins are not dominant species for most product groups with the same carbon number under the present conditions, except the C₁₂ group in which 1-dodecene yield was higher than dodecane for 30 min run.

Scheme III. Possible Mechanisms of Pyrolysis of n-Alkanes C_mH_{2m+2}



The differences between the present and literature results can be explained as follows. At high temperature ($\geq 550^\circ\text{C}$)-low pressure-short residence time (< 1 min) conditions, as employed in most previous pyrolysis work, radicals tend to undergo β -scission, which leads to products rich in 1-alkene and ethylene. Analytical data show that pyrolysis under our conditions (about 3.4-8.9 MPa system pressures at 450°C for 0-4 h) leads to more alkanes, which can be rationalized based on the Fabuss-Smith-Satterfield mechanism. Under high-pressure conditions, which in general tend to enhance bimolecular reactions, β -scission (eqs. 4,5) will be in competition with hydrogen abstraction (eq.6). Because C₈-C₁₂ alkanes and alkenes were still the major components in liquid products after 30 min at 450°C, it is likely that

the first radical formed by β -scission of $C_{14}H_{29}^{\bullet}$ radicals (eqs. 4,5) will already prefer to undergo hydrogen-abstraction (eq. 6), which yield one 1-alkene molecule and one alkane molecule. The activation energy required for H-abstraction by a radical from a hydrocarbon or molecular H_2 is smaller than that required for β -scission of the same radical. For example, the energy for β -scission of $1-C_5H_{11}^{\bullet}$ to form $1-C_3H_7^{\bullet}$ plus C_2H_4 is 29 kcal/mol, while that for its H-abstraction from another hydrocarbon or H_2 is about 10-12 or 15-17 kcal/mol at 427°C (Allara and Shaw, 1980).

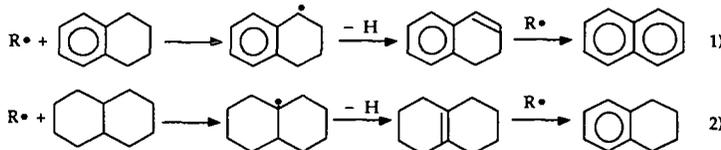
II. H-Transferring Pyrolysis and Inhibition of Solid Formation

The present work on H-transferring pyrolysis seeks to clarify whether and how the hydrogen-donors affect the pyrolytic degradation and solid-forming tendencies of jet fuel components. Figure 7 shows the inhibiting effect of tetralin on solid deposit formation from JP-8P fuel, n-C₁₄, and n-BB, respectively, at 450°C for 4 h. In the absence of H-donor, the amounts of deposits formed were n-BB (5.6 wt%) > JP-8P (3.1 wt%) \geq n-C₁₄ (3.0 wt%). These figures are extremely large if one considers the deposit formation inside fuel lines in aircraft. It is clear from Figure 3 that adding a small amount of tetralin significantly reduced the deposit formation from all these compounds. As for the efficiency of H-donor, adding 10 vol% tetralin to JP-8, n-C₁₄ and n-BB reduced the formation of deposits by 90% (from 3.1 to 0.3 wt%), 77% (from 3.0 to 0.7 wt%) and 54% (from 5.6 to 2.6 wt%), respectively. These results demonstrate that by means of H-transferring pyrolysis, hydrocarbon jet fuels can be used at high operating temperatures in pyrolytic regime with little or no solid deposition.

Multi-ring cyclic alkanes such as decalin can also serve as H-donors at high temperatures, although decalin is not as active as tetralin for inhibiting solid formation (Song et al., 1991c). Table 1 shows that decalin can also suppress the deposit formation from JP-8P jet fuel, n-C₁₄ and n-BB. In fact, adding both trans- and cis-D by 50 vol % almost eliminated solid formation from n-C₁₄, JP-8P, and n-BB. Since decalin and n-C₁₄ are also representative components of coal- and petroleum-derived jet fuels, respectively, their mixture can also be viewed as a fuel blend. These results also account for the fact observed in previous work that the presence of significant amounts of C₁₂-C₁₈ in coal-derived JP-8C did not cause remarkable solid formation (Song et al., 1991b, 1992a).

Based on the foregoing, the reduced solid formation and the enhanced stability of hydrocarbons in H-transferring pyrolysis can be attributed to the stabilization of the reactive radicals via hydrogen-abstraction from tetralin or decalin type compounds, which contributes mainly to inhibiting the secondary radical reactions and suppressing solid formation, as shown in Scheme IV.

Scheme IV. Radical Stabilization via H-Transfer from Tetralin and Decalin



We further examined the effect of adding 10 vol% H-donor tetralin on pyrolysis of n-C₁₄, n-BB, n-BCH, and cis-D at 450°C for 0.5 h (Table 1). Adding tetralin significantly suppressed the n-C₁₄ decomposition, and its conversion decreased from 49 to 37 mol%. Surprisingly, it was found that the yields of lower alkanes decreased more than those of corresponding 1-alkenes upon tetralin addition. For example, the ratio of 1-dodecene to n-dodecane increased from 1.6 to 2.6, and that of 1-undecene to undecane increased from 0.5 to 0.6 upon addition of 10 vol% tetralin. In long duration runs, the effect of tetralin in suppressing n-C₁₄ decomposition becomes smaller. This is because H-donors inhibit the radical-induced reactions but do not suppress the homolytic C-C bond cleavage. After 4 h, the major effects of H-donor appear to be the inhibition of solid and C₁-C₄ gas formation, as can be seen from Table 1.

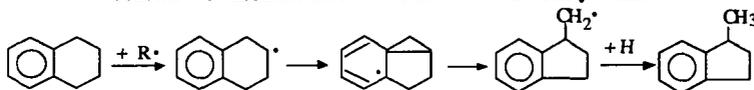
For 30 min run of n-BCH, adding tetralin decreased its conversion from about 12 to 6 mol%. In addition to the conversion decrease, the product distribution pattern changed upon tetralin addition. It was found that the decreasing extents in yields of cyclohexane, methyl- and ethylcyclohexane were higher than those for cyclohexene, methyl- and ethylcyclohexene. For cis-D, adding 10 vol% tetralin suppressed the isomerization and decomposition of cis-decalin: the conversion decreased from 12 to 8 mol%, and the cis-D/trans-D ratio increased from 14.2 to 18.9.

III. Reactions of H-donors in H-Transferring Pyrolysis

Tetralin is quite stable when stressed alone at 450°C. The major products from pyrolysis of pure tetralin are 1-

methylindan and naphthalene as well as a small amount of *n*-butylbenzene. Even after 8 h pyrolysis at 450°C, the total gas products were still within 1 wt%, indicating the ring-opening cracking and dealkylation reactions were very limited with tetralin. On the basis of the findings of Benjamin et al. (1979) and Franz et al. (1980), the isomerization proceeds through the 2-tetralyl radical to form 1-indanylmethyl radical, as shown in Scheme V.

Scheme V. Isomerization of Tetralin to 1-Methylindan



In the H-transferring pyrolysis of *n*-C₁₄ and *n*-BB, the distribution of products from tetralin shows a significantly different pattern. *n*-BB is a reactive alkylbenzene (Peng et al., 1992) As shown in Scheme VI, in the presence of *n*-C₁₄ or *n*-BB, tetralin mainly undergoes dehydrogenation reaction to form naphthalene. For the mixtures of 10 vol% tetralin with reactive compounds such as *n*-C₁₄ or *n*-BB, the ring-contraction isomerization was enhanced slightly at 450°C for 30 min but further increasing residence time increased mainly dehydrogenation. After 4 h, more than 90% of tetralin has been dehydrogenated in the case of its mixture and its isomerization was reduced significantly as compared to the run of itself. For 30 min runs, the radicals from *n*-BB were more active in dehydrogenating tetralin, although *n*-BB conversion was lower than that of *n*-C₁₄ under this condition. For the mixtures of 25 vol% tetralin with *n*-C₁₄, however, the yield of 1-methylindan from tetralin increased significantly after 4 h run, the value of which is close to that from pure tetralin.

Scheme VI. Products from Tetralin in Pyrolysis & H-Transferring Pyrolysis

Condition	Pure Tetralin		
	1-Methylindan (Me)	Naphthalene	<i>n</i> -Bu
450°C/30 min	1.7	1.3	0.2 mol%
450°C/4 h	12.7	4.0	0.5 mol%
10% Tetralin-C14	With C14 or n-BB		
	1-Methylindan (Me)	Naphthalene	<i>n</i> -Bu
450°C/30 min	5.9	4.5	mol%
450°C/4 h	90.9	5.7	mol%
10% Tetralin-BB	With C14 or n-BB		
	1-Methylindan (Me)	Naphthalene	<i>n</i> -Bu
450°C/30 min	27.1	3.6	mol%
450°C/4 h	97.0	2.3	mol%
25% Tetralin-C14	With C14 or n-BB		
	1-Methylindan (Me)	Naphthalene	<i>n</i> -Bu
450°C/4 h	64.1	12.6	mol%
25% Tetralin-BB	With C14 or n-BB		
	1-Methylindan (Me)	Naphthalene	<i>n</i> -Bu
450°C/4 h	92.3	5.6	mol%

Taking into account the difference in reaction mechanisms of dehydrogenation (Scheme IV) and isomerization (Scheme V), our results show that when the H-donor concentration is relatively low, the radicals from *n*-C₁₄ and *n*-BB mainly abstract benzylic hydrogen to yield 1-tetralyl radical. In such case, the formation of 2-tetralyl radical is very limited and hence the isomerization is not very important. This also confirms that the reactions via 1-tetralyl radical shown in Scheme IV are the major reactions. When tetralin is present at high levels, however, radicals from *n*-C₁₄ abstract hydrogens from both 1- and 2-positions. As a result, *n*-C₁₄ not only promotes tetralin dehydrogenation, but also enhances its isomerization to form 1-methylindan, although the former is still the dominant reaction. It is also interesting to note that the presence of 90 vol% *n*-BCH caused little increase in reactions of tetralin, neither dehydrogenation nor isomerization, although tetralin suppressed the *n*-BCH decomposition from 12 to 6 mol% at 450°C

for 0.5 h. On the contrary, adding 10 vol% tetralin to n-BB had little impact on n-BB conversion and gas formation at 450°C for 0.5 h, although tetralin dehydrogenation was more remarkable than in the case of n-BCH.

CONCLUSIONS

High temperature thermal stability of hydrocarbons depends mainly on their chemical structure, carbon number, length of main-chain or alkyl side-chain, and steric conformation (cis, trans). Cycloalkanes are more stable than long-chain paraffins. The stability of straight-chain paraffins decreases with increasing carbon number. Increasing the length of side-chain of alkylcyclohexanes decreases the thermal stability. Steric conformation also affects thermal reactivity, and it was found that trans-decalin is much more stable than cis-decalin.

Pyrolysis of n-tetradecane, a JP-8P jet fuel and n-butylbenzene at 450°C can result in significant amounts of solid deposits. Adding small amounts of H-donors such as tetralin and decalins was found to be effective for inhibiting fuel decomposition and solid formation at 450°C. By taking advantage of hydrogen-transferring pyrolysis reported in this work, hydrocarbon jet fuels can be used at high temperatures in pyrolytic regime with little or no solid deposition.

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REFERENCES

- Allara, D.L.; Shaw, R. J. *Phys. Chem. Ref. Data*, **1980**, *9* (3), 523-559.
Benjamin, B.M.; Hagaman, E.W.; Raaen, V.F.; Collins, C.J. *Fuel*, **1979**, *58*, 386.
Eser, S.; Song, C.; Copenhaver, R.; Parzynski, M., ACS Div. Petrol. Chem. Prepr., **1992**, *37* (2), 493-504.
Fabuss, B. M.; Smith, J.O.; Satterfield, C.N., *Adv. Petrol. Chem. Refin.*, **1964**, *9*, 158-201.
Fairburn, J.F.; Behie, L.A.; Svrcek, W.V., *Fuel*, **1990**, *69* (12), 1537-1545.
Franz, J.A.; Camaioni, D.M., *J. Org. Chem.*, **1980**, *45*, 5247-5245.
Hazlett, R.N., *Thermal Oxidation Stability of Aviation Turbine Fuels*, ASTM, 1991, and references cited therein.
Lai, W.-C.; Song, C.; Schobert, H.H.; Arumugam, R., Paper in this issue.
Peng, Y.; Schobert, H.H.; Song, C.; Hatcher, P.G., Paper in this issue.
Poutsma, M.L., *Energy & Fuels*, **1990**, *4* (2), 113-131.
Roberts, R.M.; Madison, J.J., *J. Am. Chem. Soc.*, **1959**, *81*, 5839.
Roquemore, W.M.; Pearce, J.A.; Harrison III, W.E.; Krazinski, J.L.; Vanka, S.P. *ACS Div. Petrol. Chem. Prepr.*, **1989**, *34* (4), 841.
Savage, P.E.; Klein, M.T., *Ind. Eng. Chem. Res.*, **1988**, *27*, 1348-1356.
Shabtai, J.; Ramakrishnan, R.; Oblad, A.G., *Adv. Chem. Ser.*, **1979**, *183*, 297.
Song et al., *Compositional Factors Affecting Thermal Degradation of Jet Fuels*, Technical Progress Report for Period October 1990-January 1991, Air Force Aero Propulsion Laboratory, 42-3462-TPR-2, February, 1991a.
Song et al., *Advanced Thermally Stable Jet Fuel Development Program Annual Report, Vol. 2, Final Report for Period July 1990-July 1991*, Air Force Aero Propulsion Laboratory, WL-TR-91-2117, Vol. II, August 1991b.
Song, C.; Nihonmatsu, T.; Nomura, M., *Ind. Eng. Chem. Res.*, **1991c**, *30* (8), 1726-1734.
Song, C.; Eser, S.; Schobert, H.H.; Hatcher, P.G., *ACS Div. Petrol. Chem. Prepr.*, **1992a**, *37* (2), 540-547.
Song, C.; Peng, Y.; Jiang, H.; Schobert, H.H., *ACS Div. Petrol. Chem. Prepr.*, Vol. 37, **1992b**, *37* (2), 484-492.
Zhou, P.; Hollis, O.L.; Crynes, B.L., *Ind. Eng. Chem. Res.*, **1987**, *26*, 846-852.

Abbreviations

n-BB:	n-Butylbenzene
n-BCH:	n-Butylcyclohexane
n-C10:	n-Decane
n-C14:	n-Tetradecane
cis-D:	cis-Decalin or cis-Decahydronaphthalene
trans-D:	trans-Decalin or trans-Decahydronaphthalene
ECH:	Ethylcyclohexane
JP-8P:	Petroleum-derived JP-8 jet fuel
JP-8C:	Coal-derived JP-8 jet fuel

Table 1. Deposit Formation and Liquid Depletion during H-Transferring Pyrolysis of Hydrocarbons and JP-8P Jet Fuel

Feedstocks		Condition		Products (wt%)			
Sample	+ vol% H-Donor	Temp, °C	Time, h	C1-C4 Gas	≥ C5 Liquid	Solid Deposit ^a	Recovered Deposit ^b
n-Tetradecane		450°C	4.0	38.3	58.8	3.0	1.9
Tetradecane + 50% cis-Decalin		~	~	19.5	80.3	0.1	0
Tetradecane + 50% trans-Decalin		~	~	18.2	81.7	0.1	0
Tetradecane + 10% Tetralin		~	~	27.3	72.0	0.7	0.2
Tetradecane + 50% Tetralin		~	~	9.1	90.8	0.1	0
cis-Decalin		~	~	5.4	94.6	0	0
trans-Decalin		~	~	0.8	99.2	0	0
Tetralin		~	~	0.7	99.4	0	0
n-Butylbenzene (n-BB)		~	~	17.2	77.2	5.6	5.0
n-BB + 50% cis-Decalin		~	~	14.3	85.9	0	0
n-BB + 50% trans-Decalin		~	~	12.1	87.9	0	0
n-BB + 10% Tetralin		~	~	15.4	82.0	2.6	2.5
n-BB + 50% Tetralin		~	~	9.8	90.2	0	0
JP-8P Jet Fuel		~	~	26.8	70.2	3.1	1.9
JP-8P + 50% trans-Decalin		~	~	13.3	86.6	0.1	0
JP-8P + 10% Tetralin		~	~	20.0	79.7	0.3	0.1
JP-8P + 50% Tetralin		~	~	7.9	92.0	0.1	0
n-Tetradecane		450	0.5	5.9	94.1	0	0
n-Tetradecane + 10% Tetralin		~	~	2.3	97.7	0	0
n-Butylbenzene		~	~	5.1	94.9	0	0
n-BB + 10% Tetralin		~	~	5.4	94.6	0	0
n-Butylcyclohexane		~	~	1.8	98.2	0	0
n-Butylcyclohexane + 10% Tetralin		~	~	0.7	99.3	0	0
cis-Decalin		~	~	0.3	99.7	0	0
cis-Decalin + 10% Tetralin		~	~	0.2	99.8	0	0
Tetralin		~	~	0.1	99.9	0	0

a) Solid deposit on the reactor wall determined by measuring weight gain of the microreactor after the stressing, pentane washing and drying; b) Solid deposit recovered from the reactor wall.

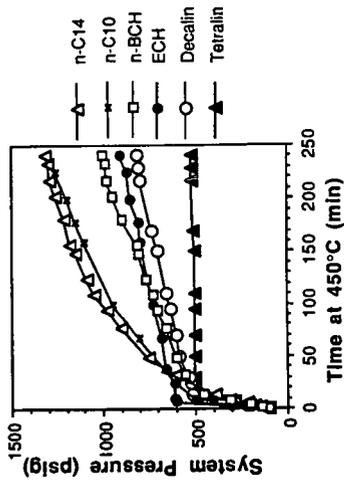


Fig. 1. System t-p profiles for pyrolysis of model compounds

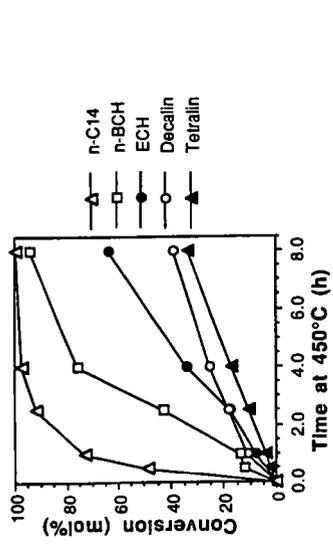


Fig. 2. Conversion of model compounds in pyrolysis

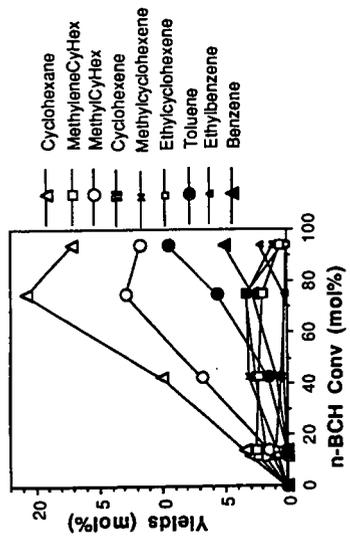


Fig. 3. Product distribution for n-BCH pyrolysis

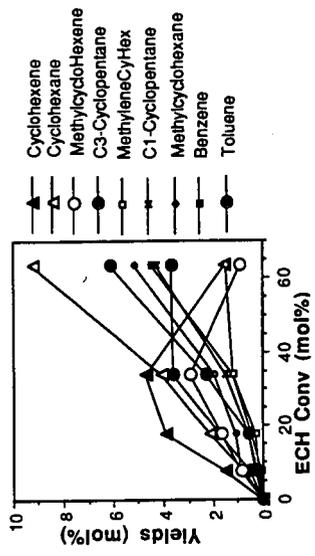


Fig. 4. Product distribution for ECH pyrolysis

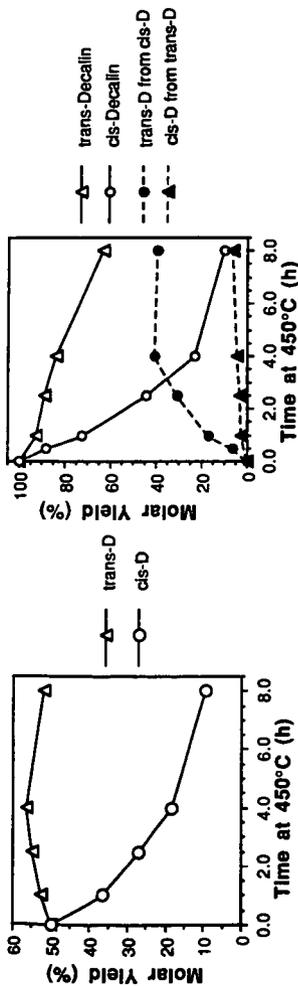


Fig. 5. Compositional change during decalin pyrolysis

Fig. 6. Conversion and isomerization during pyrolysis of pure cis-decalin and pure trans-decalin

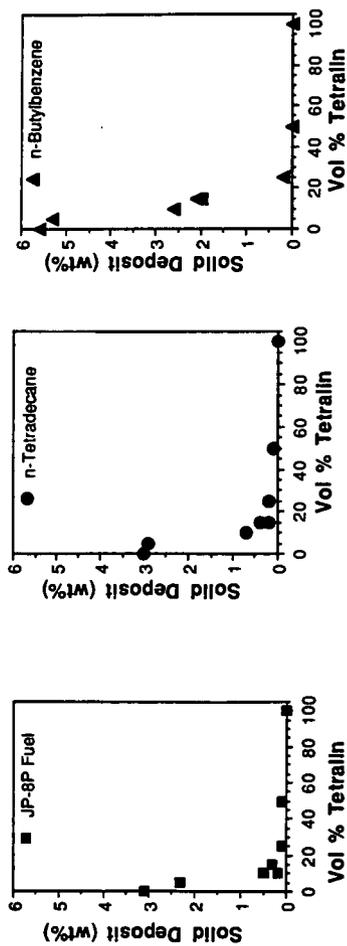


Fig. 7. Inhibiting effect of H-donor tetralin on the solid formation from JP-8P, n-tetradecane and n-butylbenzene