ADVANCED THERMALLY STABLE JET FUELS

Technical Progress Report August 1992 – October 1992

H.H. Schobert, S. Eser, C. Song, P.G. Hatcher, P.M. Walsh, M.M. Coleman

Contributions from:

J. Bortiatynski, C. Burgess, R. Dutta, K. Gergova, W-C. Lai, J. Li,
D. McKinney, D. Parfitt, Y. Peng, P. Sanghani, E. Yoon

February 1993

2
MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

for

DISCLAIMER

This report was prepared as an account of work sponsored by the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, mark manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

OBJECTIVES	1
SUMMARY	1
TECHNICAL PROGRESS	4
Task 1. Investigation of the Quantitative Degradation Chemistry of Fuels.....	4
1. Pyrolysis of Butylbenzenes: Effects of Structure of Alkyl Side Chain on the Pyrolysis of Alkylbenzenes (Contributed by Ying Peng)	4
2. Surface Effects on Carbon Deposit Formation from Jet Fuel and n-Dodecane (Contributed by Jun Li and Semih Eser).....	18
3. Effects of Hydrogen Donors on the Pyrolysis of Tetradecane at 450°C Under N ₂ Pressure (Contributed by Chunshan Song and Wei-Chuan Lai).	23
Task 2. Investigation of Incipient Deposition	33
1. Growth and Deposition of Particles During Heating of Coal-Derived Aviation Gas Turbine Fuels (Contributed by Peter Walsh and Prashant Sanghani).....	33
Task 3. Characterization of Solid Gums, Sediments, and Carbonaceous Deposits	35
1. SEM Study of the Deposits on Stainless Steel Flow Reactor Tube Surface (Contributed by Jun Li and Semih Eser).....	35
2. Effects of Adding Solid Carbons on Thermal Degradation of Jet Fuel (Contributed by Katia Gergova and Semih Eser).....	37
Task 4. Coal-based Fuel Stabilization Studies	45
1. Use of ¹³ C Labels To Trace Reactions of Potential Antioxidants for Jet Fuels (Contributed by Daniel McKinney, Jacqueline Bortiatynski, and Patrick Hatcher).....	45
2. The Mechanism of Hydrogen Transfer from Hydroaromatic Compounds—A Literature Review (Contributed by Emily Yoon)	51
Task 5. Exploratory Studies on the Direct Conversion of coal to High Quality Jet Fuels.	63
1. Production of Jet Fuels from Coal (Contributed by Caroline Burgess)	63
2. Hydrogenation/dehydrogenation Reactions of Rosin (contributed by Richard Dutta)	66
3. Temperature-programmed Liquefaction of Coals Using Bimetallic Dispersed Catalysts from Organometallic Complexes (Contributed by Chunshan Song and Derrick Parfitt).	69
Appendix.....	80

OBJECTIVES

The Penn State program in advanced thermally stable coal-based jet fuels has five broad objectives: 1) development of mechanisms of degradation and solids formation; 2) quantitative measurement of growth of sub-micrometer and micrometer-sized particles suspended in fuels during thermal stressing; 3) characterization of carbonaceous deposits by various instrumental and microscopic methods; 4) elucidation of the role of additives in retarding the formation of carbonaceous solids; and 5) assessment of the potential of production of high yields of cycloalkanes by direct liquefaction of coal.

SUMMARY

The pyrolysis of four isomers of butylbenzene was investigated in static microautoclave reactors at 450°C under 0.69 MPa of UHP N₂. The rates of disappearance of substrates were found to depend upon the bonding energy of C_α-C_β bond in the side chain in the initial period of pyrolysis reactions. Bimolecular and secondary reactions become dominant after a short period of reaction time. The rates of substrate conversion depend largely on the secondary reactions, such as H-abstraction, β-bond scission and isomerization. The pyrolysis of t-butylbenzene proceeds primarily through isomerization to i-butylbenzene and s-butylbenzene. The isomerization of t-butylbenzene to i-butylbenzene is attributed to the neophyl rearrangement induced by strains along the α-bonds in the side chain. The complex product spectrum is lumped into five groups according to their phase in the reaction and their thermal stabilities during the reactions: (1) gaseous products, including C-1 to C-4 hydrocarbon gases; (2) cracking products, including mainly benzene, toluene, ethylbenzene and C-3 substituted benzenes; (3) isomerization products, including other butylbenzenes; (4) stable high molecular weight products, including naphthalene, biphenyl, terphenyls, phenylnaphthalenes and their methyl substituted homologs; and (5) intermediate products, including mainly styrene-series compounds. Rapid conversion of a starting material does not parallel a high yield of solid products. n-Butylbenzene is quickly transformed, yet it produces the least amount of solid products. This might be because there are large amounts of cracking products, mainly toluene and ethylbenzene, formed in its pyrolysis and at the same time more stable compounds, such as naphthalene are formed. Styrene-series compounds might act as major free radical chain carriers in the sequence to form polycyclic aromatic compounds and solid products.

Possible catalytic effects of metal surfaces on thermal degradation and deposit formation at temperatures $>400^{\circ}\text{C}$ have been studied. Carbon deposition depends on the composition of the metal surfaces, and also depends on the chemical compositions of the reactants. Thus for Jet-A and n-dodecane, the effects of the same kind of metal surfaces on the formation of carbon deposit are found to be different. Carbon deposition is also related to the transfer properties of the reaction system. The structure of the deposit provides clues to the competition of different reaction mechanisms (i.e., surface carbon vs. gas-phase carbon deposition).

Addition of tetralin to n-tetradecane significantly suppressed its decomposition. For example, the presence of 10 vol. percent tetralin suppressed the decomposition of n-tetradecane by about 31% after 21 minutes at 450°C , and by about 42% after 30 minutes.

Thermal stressing of JP-8 was conducted in the presence of alumina, carbonaceous deposits recovered from earlier stressing experiments, activated carbon, carbon black, and graphite. The addition of different solid carbons during thermal stressing leads to different reaction mechanisms. Activated carbon, carbon black, and graphite prevent solid deposition during thermal stressing of JP-8 at 450°C for five hours. Alumina and the deposit obtained from previous thermal stressing result in a considerable increase in the amount of carbonaceous solid. In fact the previously produced deposits form an even greater yield of solids than alumina, even though alumina has acidic sites that can act as strong centers for catalyzing cracking reactions.

^{13}C NMR spectroscopy, along with ^{13}C -labeling techniques, have been used to examine the thermal stability of a jet fuel sample mixed with 5% benzyl alcohol. A Jet A-1 fuel laced with α - ^{13}C -labeled benzyl alcohol was thermally stressed in a manner that was reported previously. ^{13}C labeling at the α position of the benzyl alcohol makes it possible to clearly follow the reaction pathway of the labeled α carbon in the presence of complex mixtures of hydrocarbons whose carbons are at natural abundance levels (1%). ^{13}C NMR data showed that toluene and benzene were the major reaction products with the production of benzoic acid and benzaldehyde as intermediates.

Work was undertaken with the goal of developing novel bimetallic dispersed catalysts and optimum conditions for coal conversion. Several heterometallic complexes consisting of two transition metals and sulfur in a single molecule were synthesized and tested as precursors of bimetallic dispersed catalysts for liquefaction of a Montana subbituminous and Pittsburgh #8 bituminous coals. It was found that both the ligands to the metal species and the type of bonding between the two metals affect the activity of the resulting catalyst significantly. Among the M-M' type precursors tested, Co-Mo thiocubane, $\text{Mo}_2\text{Co}_2\text{S}_4(\text{Cp})_2(\text{CO})_2$ [Cp = cyclopentadiene], produced the best catalyst.

The performance of the Co-Mo bimetallic sulfide catalyst was further enhanced in temperature programmed liquefaction.

TECHNICAL PROGRESS

Task 1. Investigation of the Quantitative Degradation Chemistry of Fuels

1. Pyrolysis of Butylbenzenes: Effects of Structure of Alkyl Side Chain on the Pyrolysis of Alkylbenzenes (Contributed by Ying Peng)

Introduction

Although the thermal chemistry of alkylbenzene has been extensively studied, most of the earlier work focused on the pyrolysis at low conversions and/or in the gas phase. Among the earliest work, mention should be made of those using carrier techniques (toluene or aniline as carrier gases) for the study of short chain substituted benzenes. The primary reaction mechanisms, kinetic parameters and bond dissociation energies between C_α and C_β in the side chains have been reported [1-3]. Recently, a reaction mechanism for pyrolysis of n-butylbenzene at low conversion was proposed by Freund and coworkers [4] based on a detailed kinetic modeling with no involvement of the secondary reaction. Extensive mechanistic and kinetic studies of long chain alkylbenzene have been conducted by Savage [5,6] and Billaud [10]. Two pairs of major products were identified, i.e., toluene plus N-1 (where N is the number of carbons in the alkyl side chain) carbon atom alkene and styrene plus N-2 carbon atom alkane. The work demonstrated that the most probable reactive sites in an alkylaromatic compound are at the C_α - C_β position in the side chain. Resonance stabilization of the benzene ring effectively lowers the strength of the C_α - C_β bond. The pyrolysis behavior of alkylaromatics resembles that of aromatic compounds when the side chain is short. When the side chain is longer, the pyrolysis resembles that of the long chain paraffins. The nature of the core aromatic structure also has an effect. As the number of aromatic rings increases, there is a net increase of the reaction rate, and at the same time the linkage between the alkyl group and the aromatic rings becomes easier to break due to the so-called autocatalytic effect [8].

This report focuses on the pyrolysis of four isomeric alkylbenzenes: n-butylbenzene (n-BB), isobutylbenzene (i-BB), sec-butylbenzene (s-BB) and tert-butylbenzene (t-BB) at higher pressure (0.69 MPa) and higher substrate conversions. The effects of the structure of the alkyl side chain on the pyrolysis in terms of product (gaseous liquid and solid) formation and distribution are studied in detail. The pyrolytic pathways of the four butylbenzenes and their tendencies of solid formation are discussed.

The importance of bimolecular and secondary reactions in pyrolysis at high pressure and high substrate conversions is emphasized.

Experimental

All the compounds were obtained commercially as reagent-grade chemicals and used as received. n-Butylbenzene, isobutylbenzene and sec-butylbenzene (>99% purity) were purchased from Aldrich Chemical Company. t-Butylbenzene (98% purity) was obtained from TCI America.

Thermal stressing tests were conducted in batch tubing bomb reactors. The reactors were immersed in a fluidized sand bath at 450°C. The reactor is typically loaded with 5.00 ml of model compound. The sample loaded is deoxygenated by repetitive pressurization to 7 MPa ultra high purity (UHP) nitrogen and purging for five times after the reactor is sealed. A starting pressure of 0.69 MPa was selected for each test. The reactor reached to the reaction temperature in about 6-7 minutes after immersed into the sand bath. After desired reaction duration, the reactor was removed from sand bath and quenched in cold water to ambient temperature.

The pressure of the headspace gas in the quenched reactor was measured by a digital pressure meter connected to the reactor by a needle valve. The total volume of gases in reactor V_0 (ml, STP) was calculated by the ideal gas equation. The amount of actual product gas (total product volume V_{total} (ml, STP)) was thus obtained by subtracting from V_0 the amount of UHP N_2 initially filled in the reactor (STP). The headspace gas was collected in a gas sampling bag for GC analysis. A computerized Perkin Elmer Autosystem GC with dual detectors (FID and TCD) was used for the analysis of headspace gases. The FID detector is connected to a 6 feet long, 1/8 inch diameter stainless steel column packed with 80/100 Chemipack C18. The TCD detector was connected to a 10 feet long, 1/8 inch diameter stainless steel column packed with 100/200 carbosieve SII (Supelco). The gaseous products were calibrated by the hydrocarbon standard gas mixtures from Supelco company. The molar yield (%) of a gaseous product was calculated from the calibrated GC peak area percent ($A\%_{\text{cal}}$), and total product volume (V_{total}) via:

$$\text{Molar Yield (\%, gaseous product)} = \left(\frac{A\%_{\text{cal}} \times V_{\text{total}}}{22400} \right) / N_s$$

where N_s is the number of moles of starting material.

Most of liquid products were easily collected after each reaction. The rest of the liquid products were collected by washing with pentane. The amount of solid deposits was thus operationally defined as the materials which are not soluble in the resulting

quenched liquid co-products and pentane (washing solvent). The compounds in liquid products were analyzed using a Perkin Elmer 8500 GC equipped with a 30-meter long 0.25 mm i.d. DB-17 fused-silica capillary column (50% phenyl, 50% methyl silicone with a film thickness of 0.25 μm) and a flame ionization detector. A Hewlett Packard model 5890 Series II GC equipped with the same capillary column coupled with a model 5971A mass selective detector (MSD) was used for the identification of the compounds in the liquid products. Standards containing similar components as the liquid products were injected and the weight response factors varied only to a small extent. This probably arises from the fact that most of the compounds in the liquid are still alkylbenzenes (as discussed later in the paper). It is generally agreed that compounds having similar structures respond similarly in FID detectors [9]. For convenience, the weight response factors are assumed to be equal for all components in liquid products. Therefore, the integrated area percent ($A_i\%$) is regarded as the weight percent ($W_i\%$). According to this, the molar yield of a compound in a liquid product was calculated directly from its concentration in liquid ($W_i\%$), molecular weight (MW_i) and the total weight of the liquid product (W_{liquid}) via:

$$\text{Molar Yield (\%, gaseous product)} = \left(\frac{W_i \% \times W_{\text{liquid}}}{MW_i} \right) / N_s$$

The reaction pathways of decompositions of butylbenzenes were determined on basis of the different "selectivities" of characteristic products. Selectivity is defined in the paper as follows:

$S_A(i)$ = number of moles of i produced / number of moles of A transformed
and $S_A(i)$ is the selectivity of feed A (butylbenzenes) for product i .

Results and Discussion

1. Rate of disappearance of substrate compounds. Figure 1* presents the curves of the disappearance of butylbenzenes with reaction time pyrolyzed at 450°C. It is expected that the reactions of each compounds initially proceed through the most thermodynamically favorable bond homolysis path to form resonance stabilized benzyl or benzylic-type radicals:

*All of the figures for this report will be found in Appendix A-1.

At first glance, one might be surprised that t-BB actually decomposes more slowly than the other three isomers. In the earlier studies, alkylbenzenes were pyrolyzed using carrier techniques [10] and very low pressure pyrolysis [4]. Most of these studies were directed towards the measurement of either heats of formation of radicals, such as benzylic-type radicals and corresponding alkyl radicals, or the calculation of $\text{C}_\alpha\text{-C}_\beta$ bond dissociation energies (BDE) in the side chain of the alkylbenzenes. One of the most important factors that determines the accuracy of the data obtained was the elimination of the secondary reactions as much as possible. It was shown by the flow techniques using toluene as a radical scavenger [10,11] that n-BB had an activation energy significantly higher than t-BB. This is exactly the opposite to our results.

Calculations of bonding energies at 450°C of α (alkyl-aryl) and β ($\text{C}_\alpha\text{-C}_\beta$) bonds in the side chains of butylbenzenes gave the results in Figure 2. The calculations were based on the research by Benson [12-15], McMillen and Golden [16] and Tsang [17-19]. Although the BDE value for t-BB is a little lower than that for the other three isomers, the difference is not significant compared to the large scattering of the thermodynamic data (usually ± 2 kcal/mol).

The differences in the rate of the disappearance of the reactants must be because of factors other than bonding energies. In the present study, the reactions were carried out at 450°C under 0.69 MPa N_2 over-pressure. This high pressure makes it highly possible for the occurrence of secondary reactions after a short period of reactions. There seemed to be little difference in the rate of pyrolysis within the first 15 min (Fig. 1). Since all the four compounds have similar bonding energy at the β -position, they show similar rates of reaction. As the reactions proceed, bimolecular or even secondary reactions become more important. Typical bimolecular reactions include β -bond scission and H-abstraction with the latter being preferred in a high pressure system [20]. The H-abstraction and β -bond scission reactions that are most probably happening in the reactor are listed below:

H-abstraction:

β -bond scission:

There are several unique characteristics in the reactions regarding t-BB. The $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{CH}_2\cdot$ radicals formed in reaction (i) are not resonance-stabilized radicals, as are formed in reactions (f), (g) and (h). It can be inferred that the rate of reaction (i) would be either unfeasible or significantly slower than the others. On the other hand, all the benzylic or benzylic-type radicals formed after H-abstraction reactions in (f), (g) and (h) can easily undergo β -bond scission to form styrene series compounds according to reactions (j), (k) and (l). It is obviously not possible for t-BB to react in a similar way because of the lack of benzylic-hydrogen or β -hydrogen in $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{CH}_2\cdot$ radicals. This is probably the reason for its low reactivity.

It appears that the rates of secondary reactions mentioned above play a dominant role in the pyrolysis of butylbenzenes at later stage. It, therefore, can be understood that there are larger difference in the rates of substrate conversion in the pyrolysis after 15 min.

2. Tendencies of solid deposit formation from butylbenzenes. Shown in Figure 3 are the yields of solid products formed between 0 and 8 h. Figure 3 shows that each compound has a different induction time for the formation of solid products. This induction period reflects the ability of the compound to resist the formation of solid products. As shown in Figure 1, t-BB has the longest induction time and n-BB has the shortest. The order of the induction period for the four compounds is n-BB < s-BB < i-BB < t-BB. This order is the same as that of the rate of their disappearance. The amounts of the solids formed increase with the reaction time for s-BB, i-BB and t-BB, and their rates of increase are similar. This behavior is similar to that of jet fuels, which also exhibit monotonic increases in the amount of solid products [21]. Surprisingly, although solid products are quickly formed in the pyrolysis of n-BB, the rate of their formation is significantly lower than that of the other three isomers and the amounts almost leveled off to an asymptotic value around 5 h. As a result, the least amounts of solids are formed

from the reactions of n-BB after 8 h at 450°C. These patterns of solid formation are certainly correlated to the reaction kinetics of individual compounds. The differences in the compositions of gaseous and liquid products might be responsible for the different behaviors in their solid formation, as discussed below.

3. Product distribution and lumping of major products. Table 1 provides an overall picture of the molar yields of the major gaseous and liquid products from the pyrolysis of butylbenzenes at 450°C for 1 hour. It appears that the complex mixture of hundreds of compounds in the gaseous and liquid products can be lumped into five groups: gaseous products, cracking products, isomerization products, stable high molecular weight products, and intermediate products, according to their phase in the reactor and in situ thermal stabilities during reactions.

Group 1, gaseous products: One of the characteristics of the gaseous products formed is that only a small amount of ethylene (Table 2) is produced as compared to that formed in most of flow reactors. This may be a result of suppression of β -bond scission in closed static reactors. β -Bond scission usually has a higher activation energy (-30 kcal/mol) than H-abstraction (-10 kcal/mol). Under high pressure and a temperature such as 450°C, β -bond scission is suppressed and H-abstraction reaction is favored. According to the Fabuss-Smith-Satterfield mechanism [22], free radicals initially formed, such as benzylic, methyl and ethyl radicals, would tend to become stabilized by H-abstraction from hydrocarbon molecules. The other feature is the increase in the amount of paraffinic gases (CH_4 , C_2H_6 and C_3H_8). The amounts of olefinic gases (C_2H_4 and C_3H_6) appear to either go through a maximum or decrease in the amounts depending on the time of stressing.

The most abundant gaseous products formed are C_2H_6 for n-BB and CH_4 for s-BB, i-BB and t-BB. The formation of C_2H_6 from n-BB might be a result of H-abstraction reaction of C_2H_5 radicals produced in reaction (j). The generation of CH_4 from s-BB, i-BB and t-BB might be from reactions (e), (k) and (l), respectively. The formation of these gases is consistent with the mechanism proposed from reaction (a) to (l) and the fact that reactions (a), (c), (d) and (e) are the dominant initiation reactions. There seems to be a relatively high proportion of i- C_4H_8 formed in the pyrolysis of t-BB, especially at the short stressing times. This is probably because that the aryl-alkyl bonds in t-BB are weakened by the presence of the bulky t-butyl group, as predicted by thermodynamics (Figure 2). As a result, it is easy for an H atom to attack the ipso position of t-BB to form benzene and i-butyl radicals, or i- C_4H_8 by subsequent H abstraction as shown in reaction (l). As shown below, there is a significantly higher amount of benzene produced at the same extent of reaction as compared with other isomers.

Table 1. Molar Yields (%) of Major Products from the Pyrolysis of Butylbenzenes

Compounds	n-BB	s-BB	i-BB	t-BB
CH ₄	2.90	35.21	17.89	3.50
C ₂ H ₆	19.89	3.28	1.17	0.02
C ₂ H ₄	0.11	1.27	0.15	0.05
C ₃ H ₈	1.1	0.52	2.04	0.04
C ₃ H ₆	2.15	0.28	5.49	0.02
i-C ₄ H ₁₀				0.11
Benzene	0.36	0.27	0.33	0.35
Toluene	27.25	2.25	9.05	0.37
Ethylbenzene	13.04	8.57	1.21	0.06
Styrene	1.30	0.27	0.38	
Isopropylbenzene	0.93	11.35	0.35	0.50
n-Propylbenzene	1.16	2.28	2.22	0.06
Allylbenzene		0.12	0.40	
t-Butylbenzene		0.03	ND	85.63
i-Butylbenzene	0.39	0.05	66.23	3.11
s-Butylbenzene	1.18	55.13	0.41	0.55
α-Methylstyrene		0.31	0.11	0.36
2-Methylstyrene	0.13		1.89	0.21
Methylpropenylbenzene		0.97	0.32	0.14
n-Butylbenzene	37.10	ND	ND	
Trans-β-methylstyrene		2.20	7.10	0.73
t-Butyl-3-methylbenzene				0.03
C ₅ -Benzene	0.25	0.37	0.08	
α-Ethylstyrene		1.01		
Dimethylstyrene		1.86	0.16	0.01
Methylindans	0.21	0.08	0.25	0.20
2-Allyltoluene	1.18		0.80	
4-Ethylstyrene		0.12		
C ₆ -Benzenes	0.13			
Methylindenes		0.24	0.09	
Cyclopentylbenzene	0.24	0.07		
Naphthalene	1.39	0.26	0.61	
C ₇ -Benzenes	0.47			
2-Methylnaphthalene	0.15	0.09	0.13	0.02
1-Methylnaphthalene	0.29	0.21	0.09	
2-Ethyl-naphthalene	0.04	0.06		
Biphenyl	0.14	0.10	0.06	0.02
1-Ethyl-naphthalene	0.03	0.05		
Dimethylnaphthalene		0.10	0.05	
Diphenylmethane	0.19	0.07	0.07	
Methyibiphenyls	0.11	0.06	0.07	
Methyl-t-butylbiphenyls				0.05
Di-t-Butylbiphenyls				0.06
C ₂ -Biphenyls		0.13	0.03	
Bibenzyl	0.30	0.11	0.09	
Diphenylpropanes	0.36		0.02	

Table 1 Continued

Fluorene		0.01	0.04	
Diphenylbutanes	0.39			
Diphenylethylenes		0.11		
Diphenylhexanes	0.92			
1-Phenylnaphthalene	0.19			
Terphenyls	0.11	0.31	0.04	
2-Phenylnaphthalene	0.07	0.12	0.04	0.05

ND: not determined because it coelutes with other peaks.

Table 2. Molar Yields (mol%) of Major Gaseous Products in the Pyrolysis of Butylbenzenes

	Time (hr)	n-BB	s-BB	i-BB	t-BB
CH ₄	0.25	0.08	5.10	4.23	0.50
	1.00	2.90	35.21	17.90	3.50
	4.00	8.70	80.08	53.42	26.24
C ₂ H ₆	0.25	1.50	0.37	0.05	0.00
	1.00	19.89	3.28	1.17	0.02
	4.00	33.74	11.59	8.07	1.21
C ₂ H ₄	0.25	0.24	0.58	0.02	0.02
	1.00	0.11	1.27	0.15	0.05
	4.00	0.06	1.03	8.07	0.36
C ₃ H ₈	0.25	0.00	0.05	0.18	0.00
	1.00	1.05	0.52	2.04	0.04
	4.00	3.27	2.15	12.3	0.54
C ₃ H ₆	0.25	0.40	0.00	1.25	0.01
	1.00	2.15	0.28	5.49	0.20
	4	2.11	0.31	3.44	0.36
i-C ₄ H ₈	0.25				0.00
	1.00				0.11
	4.00				0.2

(1)

There is a relatively high proportion of C_2H_6 produced in the pyrolysis of s-BB, indicating that reaction (b) occurs as another type initiation reaction, although it is not as important as reaction (c).

Group 2, cracking products: (including mainly benzene, toluene, ethylbenzene and C_3 -substituted benzenes.) The pyrolyses of the four butylbenzenes lead to the formation of significant amounts of cracking products [23], the molecular weights of which are smaller than that of the starting materials [24]. Shown in Figure 4 are the selectivity diagrams of the major cracking products. Small amounts of benzene were formed from the pyrolysis of the four butylbenzenes. Selectivities for benzene (Figure 4(a)) are generally less than 0.05 with that for t-BB significantly higher than the other three probably due to the reasons mentioned above. Selectivities for toluene (Figure 4(b)) are relatively high among the cracking products. Selectivity for toluene is the highest for n-BB. The formation of toluene from n-BB and i-BB arises directly from the breaking of β -bonds in their alkyl side chains and the H abstraction reaction of benzyl radicals thus produced. In case of t-BB, however, toluene formation is largely attributed to its isomerization reactions to i-BB, as described later in the paper. It seems obvious that there is only a small amount of toluene generated from s-BB from a complex process probably involving more secondary reactions. It should be noted that the main sources of toluene from the pyrolysis of butylbenzenes are benzyl radicals. The large amount of toluene detected in the liquid products indicates that there might be a relatively low energy barrier for benzyl radicals to abstract H atoms. It is well known that alkyl radicals are much more reactive than benzyl radicals due to the high resonance stabilization energy of the latter [25]. Therefore, it is speculated that the H abstraction reactions by benzyl radicals are facilitated by the high pressure. It is interesting to notice in Figure 4(c) that the i-BB and t-BB have almost same selectivities for ethylbenzene, indicating that both compounds might experience similar mechanisms in forming ethylbenzene, although ethylbenzene is produced indirectly by secondary reactions from them. The formation of ethylbenzene from s-BB can be explained by reaction (b). Pathways to ethylbenzene from n-BB is not clear so far. One possible explanation is the rapid hydrogenation of styrene [8,24] produced from reaction (j). Similar arguments stand for the explanation of selectivity diagrams Figure 4(d) and (e). Attention should be paid to

the fact that C-3 substituted benzenes are not stable at the later stages of pyrolysis. At high levels of conversions, the amounts of C-3 substituted benzenes decrease in concentration.

Group 3, isomerization products: Isomerization reactions have been observed to exist in the pyrolysis of butylbenzenes:

Generally, there are two competing sets of reactions in the pyrolysis reactions at the initial stage, i.e., isomerizations and the characteristic breakdowns of each specific compound. For the pyrolysis of n-BB, i-BB and s-BB, the dominant reactions are their breakdowns. The isomerization reactions only proceed to a limited extent. As an example of isomerization reactions, Figure 5 shows the selectivities of i-BB and s-BB from the pyrolysis of n-BB. Isomerization reactions appear to be particularly important in the pyrolysis of t-BB. $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{CH}_2\cdot$ radicals generated from reaction (i) seem to have no way to react except via isomerization. There exists quite a large extent of isomerization reactions in the pyrolysis of t-BB (Fig. 5). The major isomerization product is i-BB. Only a small amount of s-BB is detected. The isomerization to i-BB in the pyrolysis of t-BB is probably initiated by $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{CH}_2\cdot$ radicals. The strain induced by the bulky t-butyl group weakens the α -bonds in t-BB molecule as predicted by thermodynamics (Fig. 2). This makes the neophyl rearrangement shown in reaction (m) [26] feasible. This mechanism is also applied to explain the isomerizations between tetralin and 1-methylindan [27,28] and bibenzyl and 1,1-diphenylethane [29,30]. It is much more difficult for n-BB, i-BB and s-BB to perform the similar rearrangement because of their stronger α -bonds. As a result, isomerization reactions are insignificant for them. The last step in reaction (m) can be achieved either by disproportionation reaction or H-abstraction reaction.

(m)

Group 4, stable high molecular weight products: (including naphthalene, biphenyl, terphenyls, phenylnaphthalenes and their methyl substituted counterparts). The concentrations of compounds in this group exhibited a monotonic increase during thermal stressing. It can be inferred that these compounds are quite stable, in the sense that their amounts accumulate with reaction time. In other words, these compounds might be inactive during the polycondensation reactions. This behavior of the compounds in the group is best exemplified by naphthalene (Figure 6), the most abundant stable high molecular weight compound produced. Other compounds, such as biphenyl, methylbiphenyls, terphenyls, methylterphenyls and phenylnaphthalenes, were produced only in small quantities. It can be seen from Figure 6 that n-BB produces the highest amount of naphthalene. This process might be associated with the H abstraction of radicals from δ position in the side chain of n-BB followed by cyclization and dehydrogenation reaction. The formation process of naphthalene from i-BB, t-BB and s-BB involves complex secondary reactions not yet clearly understood.

Group 5. intermediate products: (including mainly styrene-series compounds). The amounts of these compounds passed through maxima during relatively long stressing times. In this sense, they might be reactive during the pyrolysis reactions. They may be easily attacked by radicals (typically alkyl and benzylic radicals) and generate new larger radicals. It is expected that most of the styrene-series compounds can readily be involved in free radical chain reactions. A net result of this is to increase the free radical chain length and molecular weights of the compounds formed. Typical styrene-series compounds formed are listed in Table 3. Only styrene was detected in the liquid products from n-BB. It has already been argued that there exists a rapid transition between styrene and ethylbenzene. Although it is possible that styrene also acts as a reactive chain carrier to form higher molecular weight products at same time, a rapid transition to ethylbenzene might be an effective way to consume reactive radicals and the product (ethylbenzene) is essentially inert at the reaction temperature employed. This is probably why n-BB is consumed very rapidly during pyrolysis, while the formation of solid deposit does not follow the same trend. Naphthalene, toluene, and ethylbenzene can be easily produced in large amounts in the pyrolysis of n-BB. Once these compounds are formed, it is difficult for them to re-enter the free radical chain since they are basically unreactive at 450°C. On the other hand, it is clear from Table 3 that there are various of styrene-series compounds formed in the pyrolysis of s-BB, i-BB and t-BB. There exist some common characteristics in i-BB and t-BB pyrolysis in that major intermediate compounds are the same. Both compounds have trans- β -methylstyrene and 2-methyl-1-propenylbenzene as

major styrene-series compounds formed. Trans- β -methylstyrene can be produced through reaction (l) for both i-BB and n-BB and 2-methyl-1-propenylbenzene might be from the disproportionation reaction of isobutylbenzene radicals in reaction (m). Similar arguments can be made to rationalize the intermediate products formed in the pyrolysis of s-BB. For example, trans- β -methylstyrene originated from direct breakdown of s-BB and subsequent H-abstraction. It appears that the existence of the varieties of intermediate products in the pyrolysis of s-BB, i-BB and t-BB significantly facilitated the polycondensation reactions to form polycyclic aromatics and finally carbonaceous solid products. There are small amounts of bibenzyl produced in the pyrolysis, as shown in Table 3. The role of bibenzyl in the formation of PAH and solid products is not well understood. Model compound studies [29,30] of liquid-phase pyrolysis demonstrated that primary reaction products are toluene, stilbene, 1,1-diphenylethane and a small amount of phenanthrene. These are also detected in the present study, but in a much lower concentration, because the bibenzyl itself was formed in limited quantities.

It should be mentioned that there exists a large degree of "chain re-synthesis" reactions at the early stage of pyrolysis. The products are pentylbenzenes, hexylbenzenes and heptylbenzenes. They were probably formed by simple combination of alkyl radicals and benzyl (benzylic) radicals facilitated by high pressure. These compounds are even less stable than the starting materials. They disappeared completely at relatively longer reaction times. There are also small amounts of di-t-butylbiphenyls and methyl-t-butylbiphenyls detected in the liquid of t-BB pyrolysis. The exact processes of their formation are complicated and not well understood but probably indicates that the presence of t-butyl group activates the benzene ring to some extent so that the reactions through the ring can proceed to a certain degree.

Conclusions

The structures of the side chain in alkylbenzenes significantly affect their reactivities and solid formation tendencies. In the initial short period of pyrolysis, the pyrolysis reactions were controlled by rate of the unimolecular dissociation processes of $C_{\alpha}-C_{\beta}$ bonds in the side chains. The four compounds studied exhibited similar rates of disappearance initially, because of their similar $C_{\alpha}-C_{\beta}$ bonding energies. After the initial period of reaction, the rates of the disappearance of the substrates are determined by the secondary reactions other than the one mentioned above because of the presence of high pressure. The order of reactivity was found to be $n\text{-BB} > s\text{-BB} > i\text{-BB} > t\text{-BB}$ in terms of their rates of the consumptions.

Table 3. Molar Yields (%) of Major Intermediate Products

Material	Compounds identified	Time (hr)			
		0.25	1	4	8
n-BB	styrene	3.94	1.30	0.31	0.23
	bibenzyl	0.00	0.29	0.08	0.05
t-BB	α -methylstyrene	0.20	0.36	0.31	0.21
	trans- β -methylstyrene	0.01	0.73	0.20	0.15
	2-methyl-1-propenylbenzene	0.07	0.14	0.46	0.38
	2-methylstyrene	0.06	0.21	0.73	0.49
i-BB	styrene	0.02	0.38	0.14	0.11
	allylbenzene	0.08	0.4	0.03	0.03
	α -methylstyrene	0.09	0.10	0.11	0.10
	2-methylstyrene	0.80	1.89	0.25	0.10
	2-methyl-1-propenylbenzene	0.01	0.32	0.19	0.05
	trans- β -methylstyrene	3.21	7.10	0.74	0.25
	2-allyltoluene	0.12	0.80	0.66	0.11
	bibenzyl	0.00	0.10	0.10	0.05
s-BB	styrene	0.14	0.27	0.18	0.18
	allylbenzene	0.08	0.12	0.00	0.00
	α -methylstyrene	0.11	0.31	0.21	0.00
	ethylstyrenes	0.02	0.16	0.28	0.10
	1-methyl-1-propenylbenzene	0.07	0.10	0.13	0.05
	trans- β -methylstyrene	0.79	2.20	0.83	0.37
	α -ethylstyrene	0.17	1.01	0.08	0.03
	dimethylstyrenes	0.17	1.86	0.24	0.08
	methylindenes	0.00	0.23	0.20	0.12
	bibenzyl	0.00	0.11	0.07	0.04

Isomerization reactions occur during the pyrolysis of butylbenzenes in competition with the characteristic breakdown of individual compounds. Isomerization play an important role in the pyrolysis of t-BB. It showed a large extent of isomerization to i-BB, and to s-BB to a lesser extent. It is proposed that the mechanism to form i-BB is through a so-called neophyl rearrangement process caused by the strains in the α -bonds of t-BB. The mechanism helps to explain the low reactivity of t-BB and some similar behavior between the pyrolysis of i-BB and t-BB.

In a whole spectrum of products, cracking products, such as benzene, toluene and ethylbenzene are stable at 450°C. C-3 substituted benzenes are unstable only at very high conversions. High molecular weight products, such as naphthalene, biphenyl, methylbiphenyls, terphenyls, methylterphenyls and phenylnaphthalenes seem to be "inactive" or "passive" in the pyrolysis. Unless attacked by very reactive radicals, they are probably quite stable. Styrene series compounds, on the other hand, can easily be

involved in chain reactions to form large radicals. This type of compounds may be unstable intermediate compounds which facilitate the polycondensation reactions and therefore solid product formation.

It appears necessary to differentiate the reactivity (defined in rate of substrate consumption) of a compound and its solid formation tendency. It is the properties of product mixture formed during the on-going reactions that determines the solid formation tendency. Although n-BB is quickly disappeared during pyrolysis, it is not the one that forms highest amounts of solids because it produces significant amounts of cracking products, such as toluene and ethylbenzene and stable high molecular weight products, such as naphthalene. On the other hand, less styrene series compounds are found. In contrast to this, a variety of styrene series compounds are identified in the liquids of t-BB, i-BB and s-BB, they also form higher amounts of solid products.

References

- [1] Leigh, C. H.; Szwarc, M. *J. Phys. Chem.* 1952, 20, 844.
- [2] Kerr, J. A.; *Chem. Rev.* 1966, 66, 465.
- [3] Leigh, C. H.; Szwarc, M. *J. Chem. Phys.* 1952, 20, 403.
- [4] Freund, H.; Olmstead, W. N. *Int. J. Chem. Kinetics* 1989, 21, 561.
- [5] Savage, P. E. ; Korotney, D. J. *Ind. Eng. Chem. Res.* 1990, 29, 499.
- [6] Savage, P. E.; Klein, M. T. *Ind. Eng. Chem. Res.* 1987, 26, 488.
- [7] Billaud, F.; Chaverot, P.; Berhtelin, M.; Freund, E. *Ind. Eng. Chem. Res.* 1988, 27, 1529.
- [8] Savage, P. E.; Jacobs, G. E.; Javanmardian, M. *Ind. Eng. Chem. Res.* 1989, 28, 645.
- [9] Grob, R.L., *Modern Practice of Gas Chromatography*; John Wiley & Sons, 1977.
- [10] Leigh, C.H.; Szwarc, M. *J. Chem. Phys.* 1952, 20, 407.
- [11] Banerjee, D.K.; Matei, V.; Vantu, V. *Revue Roumaine de Chimie* 1982, 27, 621.
- [12] Benson S.W. *Thermodynamic Kinetics*; Wiley Publisher: New York, 1976.
- [13] Benson, S.W.; Cruickshank, F.R.; Haugen, G.R.; O'Neal, H.E.; Rogers, A.S.; Shaw, R.; Walsh, R. *Chem. Rev.* 1969, 69, 279.
- [14] O'Neal, H.E.; Benson, S.W. *Int. J. Chem. Kinet.* 1969, 1, 221.
- [15] Benson, S.W. *Kinetic Data on Gas Phase Unimolecular Reaction* 1970, Natl. Ref, Data Serv. NSRDS-NBS 21, US Dept. Commerce.
- [16] McMillen, D.F.; Golden, D.M. *Ann. Rev. Phys. Chem.* 1982, 33, 493.
- [17] Tsang, W. *Prepr. Pap., ACS Div. Fuel Chem.* 1992, 37, 367.
- [18] Tsang, W. *J. Am. Chem. Soc.* 1985, 107, 2873.

- [19] Walker, J.A.; Tsang, W. *J. Phys. Chem.* 1990, 94, 3324.
- [20] Poutsma, M.L. *Energy Fuels* 1990, 4, 113.
- [21] Song, C.; Peng, Y.; Jiang, H. & Schobert, H.H. *Prepr. Pap. ACS Div. Pet. Chem.* ACS, 1992, 37(2), 484.
- [22] Fabuss, B.M.; Smith, J.O.; Satterfield, C.N. *Advances in Petroleum Chemistry and Refining*, Vol. IX, 1964.
- [23] Song, C.; Eser, S.; Schobert, H.H.; Hatcher, P.G; et. al., *Advanced Thermally Stable Jet Fuels Development Program Annual Report*, Volume II, Interim Report for Period July 1990 to July 1991, U.S. Air Force Aero Propulsion and Power Directorate, WL-TR-91-2117.
- [24] Peng, Y., Schobert, H.H., Song, C. & Hatcher, P.G., *Prepr. Pap. ACS Div. Pet. Chem.* 1992, 37, 505.
- [25] March, J. *Advanced Organic Chemistry, Reactions, Mechanisms, and Structure*; 3rd Edition, John-Wiley and Sons: London, 1985.
- [26] Stein, S.E. *Chemistry of Coal Conversion*; R.A. Schlosberg, Ed.; Plenum Press: New York, 1985.
- [27] Franz, J.A.; Camaioni, D.M. *Fuel* 1980, 59, 803.
- [28] Cronauer, D.C.; Jewel, D.M.; Modi, R.J.; Seshadri, K.S.; Shah, Y.T. *Coal Liquifaction Fundamentals*; D.D. Whitehurst, Ed; ACS Symposium Series, No. 139, American Chemical Society, Washington, DC, 1980, p371.
- [29] Miller, R.E.; Stein, S.E. *J. Phys. Chem.* 1981, 85, 580.
- [30] Poutsma, M.L. *Fuel* 1980, 59, 335.

2. Surface Effects on Carbon Deposit Formation from Jet Fuel and n-Dodecane (Contributed by Jun Li and Semih Eser)

Introduction

Possible catalytic effects of metal surfaces on thermal degradation of jet fuels and deposit formation at high temperatures (>400°C) have not been studied. It is generally believed that copper is the most deleterious material at relatively low temperature because it can significantly increase the amount of deposit formed on a metal surface (Taylor, 1968). Over a wider temperature range, it was found that stainless steel (type 316) tubes gave more deposit than aluminum tubes, approximately by a factor of 2 (Wong and Bittker, 1982; Kendall and Mills, 1985). Taylor (1968) suggested that the observation of copper tube producing more deposit may be due to the catalysis of oxidation reactions by oxides of copper. In the low-temperature regime, according to Hazlett (1977),

autoxidation is the dominant reaction in fuel degradation. Since thermal degradation processes at high temperatures involve principally pyrolysis reactions, rather than autoxidation reactions, one should expect different catalytic effects, if any, at high temperatures.

A systematic study of the effects of metal surface on deposit formation at high temperatures ($> 400^{\circ}\text{C}$) has been initiated in this project. Different metals such as copper (Cu), nickel (Ni), iron (Fe), titanium (Ti), stainless steel (SS), and gold (Au), among others, will be used in the form of transmission electron microscope (TEM) grids, wires, powders, and foils to study surface effects. This report presents the results of preliminary studies of the effects of metal grids and wires on the thermal stability of n-dodecane and Jet A fuel. An SEM characterization of the carbon deposit on a stainless steel tube received from Sandia National Laboratories is also presented.

Deposits Collected from the Reactor Walls

1. Thermal stressing of n-dodecane with metal grids. TEM metal grids (200 mesh) made of Cu, Ni, Ti, SS, and Au were used to study the deposits collected on different metal surfaces. The experimental conditions were kept consistent, i.e. all using 5 ml n-dodecane with an initial N_2 pressure of 100 psi, five pieces of grids at the bottom of the tubing bomb reactor, and 5 hours of thermal stressing under 450°C .

The amount of deposit collected from the reactor surface after these tests is shown in Figures 7 and 8 (weight of the carbon deposits on the grids was typically 2-3 mg in each experiment).

Figure 8 shows the average amount of solid deposits collected from the carbonization of pure n-dodecane, with SS, Ti, Au, Cu, and Ni grids. From this figure, it can be seen that the presence of SS, Au, and Ni grids increases the amount of deposit slightly, while the addition of Ti and Cu grids decreases the amount of deposit significantly.

2. Thermal stressing of Jet A with metal grids. The experimental conditions were similar to those used in n-dodecane tests. Five ml Jet A fuel was added to the tubing bomb reactor in which 8 pieces of grids were sit at the bottom. The initial N_2 pressure was again 100 psi and the temperature was kept constant at 450°C during the 5 hour test periods.

The amount of solids collected is shown in Figure 9. It can be seen that the presence of any metal grids increases the amount of deposit relative to neat Jet A. In addition, the amount of deposit collected from Jet A was higher than that from n-

dodecane. In contrast to n-dodecane stressing, the differences between different grids are not significant and within the experimental error.

3. Thermal stressing of n-dodecane and jet A with different wires. Three kinds of metal wires, Cu, Ni, and Fe, all with a diameter of 1 mm, were tested in thermal stressing experiments. Again, 5 ml n-dodecane or Jet A fuel was initially added to the tubing bomb reactor. Two segments of wire were put inside the reactor: one in 1 cm lying at the bottom of the reactor, the other in 6 cm standing against the reactor wall. Because iron wire was moisture sensitive, and copper wire was air sensitive, both of these wires were handled in a glove bag under N₂ protection. Initial N₂ pressure in the reactor was 100 psi., temperature was kept constant at 450 °C during the 5 hour test periods. The amount of deposit collected is shown in Figures 10 and 11.

Morphology of Carbonaceous Solids on Metal Grids

The surface areas of the metal grids are relatively small; therefore, the effects of these metal surfaces on the bulk chemistry and the amount of solid collected are not expected to be significant. However, the morphology of the carbonaceous deposits on the grids can provide useful information for elucidating the mechanisms of the solid deposition process. The morphology of the carbonaceous deposit on metal grids has been studied mainly by scanning electron microscopy (SEM).

1. Deposit on metal grids from thermal stressing of n-dodecane.

Cu Grids. The deposition on copper grids began with coalesced spheres on the inner edges of the square holes. Usually, the deposit grew laterally via small distinct spheres ($d = 1\ \mu\text{m}$), showing a ring by ring growth pattern. The lateral growth could be so dominant that holes of the grid are reduced and filled ring by ring before significant perpendicular growth on the frames of the grid starts.

Meanwhile, a perpendicular growth of the deposit layer by layer via small spheres was also observed. Further coalescence of the sphere deposit on the layer was observed to form larger clusters. Bulky deposit pieces were formed whenever the deposit can grow both laterally and perpendicularly. Figure 12a shows some of the features of deposit on a Cu grid.

Ni Grids. Very little deposit was formed on Ni grids. Growth of the deposit was solely lateral. Coalescence of the small spheres was vigorous resulting larger spheres of 5–17 μm diameter. Bulky deposit blocks were also found on the grids. However, these blocks did not seem to have grown from the grid, they were probably from the liquid reactions and then stuck onto the grid. Figure 12b shows some of the features of deposit on a Ni grid.

SS Grids. More deposit was found on the stainless steel grid. A clear perpendicular growth pattern could be seen. Deposit was either on the frames or on the rim of the grid. On the frames, large distinct spheres with diameter of about 5 μm were at the bottom layer. These spheres could further coalesce to give a continuous bulk deposit layer. Top layer of this deposit consisted of much smaller spheres of 0.5 μm in diameter. On the rim, deposition also started with large spheres. The coalescence of these spheres was probably less intensive than on the frame. Therefore, deposit on the rim clearly had a dispersed structure. Figure 12c shows some of the features of deposit on a S.S grid.

Ti Grids. Again, little deposit was found on titanium grids. Deposit grew mainly laterally. Moreover, the severity of this lateral growth increased from the center towards the rim of the grid. The carbon that belongs to the ring pattern deposit had a small diameter (about 0.5 μm) thus resulting in a smooth deposit front and surface. On top of this deposit disk grew another type of deposit; it started from the inner edges of the square holes, then coalesced and probably also moved laterally, and finally filled the grid holes that were close to the rim. Figure 12d shows some of the features of deposit on a Ti grid.

Au Grids. A perpendicular growth pattern was also observed with gold grids, both on the frame and on the rim of the grid. Deposit on frames grew to form a continuous layer without significant lateral stretch towards the center of the holes. A noteworthy feature was that on top layer of the deposit grew another layer of large spheres of about 10 μm diameter. Meanwhile, there were scattered finer spheres (about 0.5 μm diameter) on top layer of the deposit, and even on the surface of the large spheres, indicating a regenerative nucleation and growth mechanism. Figure 12e shows some of the features of deposit on a Au grid.

In summary, there are two types of globular carbon deposits and three distinct growth patterns observed with the metal grid tests. The globular carbon deposit consists of spheres either of 5–17 μm in diameter or of 0.5 μm in diameter. It is unlikely that the former is the agglomerates of the smaller spheres. These two types of carbon may result from different reaction or growth history, for example, surface pyrolytic carbon/liquid mesophase carbon vs. gas phase carbon. The three growth patterns include lateral, perpendicular, and combined lateral-perpendicular growth. Lateral growth was mainly found with Ni and Ti grids, perpendicular growth was found with SS and Au grids, while a combined growth pattern was observed with Cu grids. The growth patterns should be further confirmed by tests run with shorter period of thermal stressing and at lower temperatures. Figure 13 schematically shows the three growth patterns.

It is tempting to correlate the amount of deposit collected with the types of the deposit present or the growth pattern. It seems that perpendicular growth produces more deposit, and lateral growth less deposit, with Ni grids being an exception. As far as the types of deposit are concerned, more deposit is produced when there are large spheres (SS, Au, and Ni), and less deposit is produced when there are smaller spheres (Cu and Ti).

2. Deposit on grids from thermal stressing of Jet A.

Ni grids. Deposition on Ni grids was significant. Ni grids became very delicate after five hours thermal stressing at 450° C. This may be due to the formation of nickel carbide, that makes the grid brittle to handle. SEM studies on Ni pieces showed rough carbon surface with ruptured Ni grids. Figure 14a shows some of the features of deposit on a Ni grid.

Cu grids. Deposits on copper grids from Jet A was found to be different from those obtained from n-dodecane. Very fine deposit particles were dispersed on the frames and the rim. No distinct growth pattern could be identified. Much less deposit was found from Jet A than from dodecane. Figure 14b shows some of the features of deposit on a Cu grid.

Ti grids. Deposit on Ti grids was very similar to that from n-dodecane. Carbon deposit disks were formed along the square edges, which is probably due to the higher activity of the corners and edges of the grid. In addition, a dispersed carbon layer was found on top of the grids (perpendicular growth), contrasting sharply with the growth pattern in dodecane stressing. Figure 14d shows some of the features of deposit on a Ti grid.

SS and Au grids. Thick, amorphous carbon layers were found on stainless steel and gold grids. Some coalesced spheres could be identified under the carbon layer. These deposits were most likely developed via liquid phase reactions. Figure 14d and 14e show some of the features of the deposits on stainless steel and gold grids.

In summary, no distinct growth patterns similar to the thermal stressing of dodecane tests could be found in Jet A tests. Carbon morphologies on different grids indicate more severe reactions in Jet A than their counterparts in n-dodecane. This is in agreement with the actual amount of deposit collected on reactor walls in both sets of tests.

Conclusions

Some general conclusions which follow from the analyses of carbon deposits, and morphologies on metal grids are summarized below:

Carbon deposition depends on the composition of the metal surfaces. It could be surface sensitive (lateral growth as on Ni and Ti grids), or surface insensitive (perpendicular growth as on Au and SS grids), or intermediate (lateral-perpendicular combined). In terms of the amount of solid, no consistent correlation between the amount of deposit and the kind of metal grids was seen because the limited amount of tests and the experimental technique used.

Carbon deposition also depends on the chemical compositions of the reactants. For Jet A and n-dodecane, the effects of the same kind of metal grids on the formation of carbon deposit are found to be different;

Lower reaction temperatures and different metal geometries will be used in the future studies to elucidate the effects of metal surfaces on thermal degradation reactions and solid deposition.

References

- Hazlett, R.W., Hall, J.M., and Matson, M. (1977). "Reactions of aerated n-dodecane liquid flowing over heated metal surface", I & EC, Prod. Res. Dev. Vol. 16(2): p171.
- Kendall, D.R. and Mills, J.S.(1985). "The influence of JFTOT operating parameters on the assessment of fuel thermal stability", Proceedings of the aerospace technology conference and exposition, Long Beach, CA, p143.
- Taylor, W.F. (1968). "Kinetics of deposit formation from hydrocarbons, III. heterogeneous and homogeneous metal effects", J. appl. chem., Vol. 18: p.251.
- Wong, E.L. and Bittker, D.A. (1982). "Effects of hydrocarbon fuel type on fuel thermal stability", NASA-TM 82916.

3. Effects of Hydrogen Donors on the Pyrolysis of Tetradecane at 450°C Under N₂ Pressure (Contributed by Chunshan Song and Wei-Chuan Lai).

Introduction

The hydrogen-transferring pyrolysis described here refers to the thermal decomposition of hydrocarbons in the presence of H-donors. The present work is a continuation of a fundamental study of condensed-phase pyrolysis of saturated hydrocarbons including the straight-chain paraffins, alkylcyclohexanes, trans- and cis-steric isomers of decalin as well as hydroaromatics such as tetralin. 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; Hazlett,

1991; Song et al., 1993a, 1993b]. 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 of hydrocarbon components and solid formation [Song et al., 1991a, 1991b, 1992a, 1992b, 1993a].

It should be noted that the experimental conditions used in this work are such that they are close to the severity of the anticipated high-temperature thermal environment of jet fuel in the future high-Mach aircraft under consideration [Song et al., 1993a]. 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). In this quarterly report we will report on 1) the results of detailed analysis of products from pyrolytic degradation of tetradecane; 2) inhibiting effects of H-donors on the decomposition of *n*-tetradecane (*n*-C₁₄); and 3) the mechanisms of the pyrolysis and H-transferring pyrolysis of *n*-C₁₄.

Experimental

Reagent-grade normal tetradecane, *n*-C₁₄, tetralin, trans-decalin (trans-D) and cis-decalin (cis-D), and decalin (mixture) from Aldrich and a petroleum-derived JP-8P jet fuel [Song et al., 1992a, 1992b] were used. The hydrogen-donor compounds examined in this work include tetralin, decalin, cis-D and trans-D. In a typical run, 5 mL of *n*-tetradecane (about 3.8 g, 19 mmol) was charged into the reactor. For hydrogen-transferring pyrolysis, the mixture of *n*-tetradecane and a H-donor agent, usually 10 % by volume, was transferred into the reactor.

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 [Song et al., 1993a]. A fluidized sandbath preheated to 450°C was used as heater. The products were identified by capillary GC-MS and quantified by GC. More analytical details may be found in an earlier paper [Lai et al., 1992].

Results and Discussion

1. *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. Table A* shows the yields of products expressed as molar percentage based on *n*-tetradecane.

*Tables designated by letters rather than numbers are located in Appendix A-2.

There are several trends that can be seen from Table A. First, in the liquid products, there are no particular products that have high selectivity from C₄ to C₁₁. Second, in the early periods of the pyrolysis, there are very little 1-tridecene and n-C₁₃ products; there is very little n-C₁₂, and even after 30 min at 450°C, 1-dodecene is still more abundant relative to n-C₁₂. Third, the conversion of n-tetradecane (n-C₁₄) increases, but the ratio of 1-alkene to the corresponding n-alkane in the products decreases with increasing residence time. The yields of some 1-alkenes increase and reach a maximum after 1 h or 2.5 h at 450°C, then start to decrease. After 30 min at 450°C, 53 % of n-C₁₄ has been decomposed, and the main products are C₁-C₁₃ alkanes and C₂-C₁₃ 1-alkenes. Finally, the data in Table A show that in the liquid products, cyclohexanes appear before alkylbenzenes; alkylbenzenes appear before alkylnaphthalenes. This observation also supports the proposed mechanisms for solid formation from jet fuels under pyrolytic conditions in our recent paper [Song et al., 1992c]. By analyzing the product distribution and its variation with time in a quantitative fashion, we have developed a general and fundamental understanding of the reaction mechanisms for thermal cracking of long-chain n-alkanes such as n-tetradecane under the high-pressure pyrolytic conditions employed in this work.

Scheme I shows the proposed, generalized reaction mechanisms for thermal cracking of long-chain alkanes such as tetradecane under the conditions employed [Song et al., 1992d]. There is no question that under the conditions, the pyrolysis of n-tetradecane proceeds by radical reaction pathways. The initiation reaction is the homolytic cleavage of a carbon-carbon bond, producing two radicals. These radicals then abstract hydrogen from a molecule, mostly the reactant substrate itself in the initial period. The first substrate radicals from n-C₁₄ include both *sec*-C₁₄H₂₉• (eq.2) and *pri*-C₁₄H₂₉• (eq. 3). Formation of the primary radical requires slightly higher activation energy, e.g., the activation energies required for H-abstraction by a radical from n-butane to form 2-C₄H₉• and 1-C₄H₉• at 700 K are 10.4 and 12.3 kcal/mol, respectively.

It is clear from Table A that the carbon number distribution of the products from n-tetradecane is broad and there is not much selectivity. Probably there are two reasons for the largely non-selective product distribution. First, the energy to abstract any secondary hydrogen in long-chain paraffins such as n-tetradecane is about the same. This was also indicated by Ford for liquid-phase n-hexadecane pyrolysis [1986]. Second, the homolytic cleavage of long-chain alkanes is not very selective, because both the activation energy and the A-factor values are similar for the formation of different pairs of two radicals with ≥ 2 carbon atoms. Supporting evidence can be found from the Arrhenius parameters

[Allara and Shaw, 1980] for three different initiation reactions of n-hexane at 700 K, as shown in Table 4.

Scheme I. Mechanisms of Pyrolysis of n-Alkanes C_mH_{2m+2} [Modified from C. Song, W.-C. Lai, and H.H. Schobert, Am. Chem. Soc. Div. Fuel Chem. Prepr., 1992, 37 (4), 1655-1663]

Table 4. Arrhenius parameters and rate constants at 700 K for radical initiation reactions

Reactant	Products		log[A/S ⁻¹]	E	log [k/S ⁻¹]
				kcal/mol	
n-C ₅ H ₁₂	CH ₃ •	1-C ₄ H ₉ •	17.5	85.5	-9.2
n-C ₅ H ₁₂	C ₂ H ₅ •	1-C ₃ H ₇ •	17.1	81.6	-8.4
n-C ₆ H ₁₄	CH ₃ •	1-C ₅ H ₁₁ •	16.8	85.4	-9.9
n-C ₆ H ₁₄	C ₂ H ₅ •	1-C ₄ H ₉ •	16.8	81.9	-8.8
n-C ₆ H ₁₄	1-C ₃ H ₇ •	1-C ₃ H ₇ •	16.5	81.9	-9.1

Thermal decomposition of long-chain paraffins is still the subject of pyrolysis research. 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 C₁₂ for which 1-dodecene yield was substantially higher than dodecane for 6-21 min runs.

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 ethylene and 1-alkene. Such pyrolysis reactions can be described by the well-known Rice-Kossiakoff mechanism. Analytical data show that pyrolysis under our conditions (about 3.4-8.9 MPa system pressure 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 (eqs. 6, 7). Because C₈-C₁₁ 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 C₁₄H₂₉ $\cdot$ radicals (eqs. 4,5) will already prefer to undergo hydrogen-abstraction (eq. 6), which yield one 1-alkene molecule and one alkane molecule. This is probably because the activation energy required for H-abstraction by a radical from a hydrocarbon or molecular H₂ is smaller than that required for β -scission of the same radical. These reactions are shown in Schemes II and III. Supporting evidence can be found by comparing the Arrhenius parameters for H-abstraction and β -scission at 700 K [Allara and Shaw, 1980]. The activation energy for β -scission of 1-C₅H₁₁ $\cdot$ to form 1-C₃H₇ $\cdot$ plus C₂H₄ is 29 kcal/mol, while that for its H-abstraction from another paraffinic hydrocarbon or H₂ is about 10-12 or 15-17 kcal/mol.

It is also worthwhile considering the fact that in the initial stage of n-C₁₄ pyrolysis (6 min, Table A), there is very little n-dodecane, but 1-dodecene is dominant among the C₁₂ products. This is because different reaction pathways are involved in the formation of these two compounds. In the initial reaction stage, probably the m-2 paraffinic product C_{m-2}H_{2(m-2)+2} of the reactant C_mH_{2m+2} can only be formed from β -scission of a primary

Scheme II. Radical decomposition (β -scission) reactions of secondary-radical (sec-R $\bullet$) during n-tetradecane pyrolysis.

6)

 $n \neq 1$ $n \neq 2$ $n = 3$ $\text{n-C}_{11}\text{H}_{24} + \text{sec-C}_{14}\text{H}_{29}\cdot$ $n = 4$ $\text{n-C}_{10}\text{H}_{22} + \text{sec-C}_{14}\text{H}_{29}\cdot$ $n = 5$ $\text{n-C}_9\text{H}_{20} + \text{sec-C}_{14}\text{H}_{29}\cdot$ $n = 6$ $\text{n-C}_8\text{H}_{18} + \text{sec-C}_{14}\text{H}_{29}\cdot$ $n = 7$ $\text{n-C}_7\text{H}_{16} + \text{sec-C}_{14}\text{H}_{29}\cdot$ $n = 8$ $\text{n-C}_6\text{H}_{14} + \text{sec-C}_{14}\text{H}_{29}\cdot$ $n = 9$ $\text{n-C}_5\text{H}_{12} + \text{sec-C}_{14}\text{H}_{29}\cdot$ $n = 10$ $\text{n-C}_4\text{H}_{10} + \text{sec-C}_{14}\text{H}_{29}\cdot$ $n = 11$ $\text{C}_3\text{H}_8 + \text{sec-C}_{14}\text{H}_{29}\cdot$ $n = 12$ $\text{C}_2\text{H}_6 + \text{sec-C}_{14}\text{H}_{29}\cdot$ $n = 13$ $\text{CH}_4 + \text{sec-C}_{14}\text{H}_{29}\cdot$

Scheme III. Possible radical hydrogen-abstraction reactions of primary-radical (pri-R•) during n-tetradecane pyrolysis.

$\text{C}_m\text{H}_{2m+1}\cdot$ followed by hydrogen abstraction, whereas the secondary $\text{C}_m\text{H}_{2m+1}\cdot$ radical of the substrate afford the m-2 olefinic product $\text{C}_{m-2}\text{H}_{2(m-2)}$. Therefore, the above-mentioned fact also reflects that among reactions 2 and 3 in Scheme 1, the reaction 2 is dominant.

Another general trend observed in this work is that the yields of 1-alkenes including 1-dodecene decreased, whereas the corresponding n-alkanes including n-dodecane further increased with increasing time up to certain residence time, as shown in Table A. This is probably due to two kinds of reactions in later stage: 1) formation of diene from 1-alkene followed by cyclization and dehydrogenation; and 2) hydrogenation of the alkenes by the hydrogen generated in situ. The possible mechanism for olefin

hydrogenation is shown in equations 9 and 10. GC analysis indicated the presence of molecular H₂ in the gas products, and its yield increased with residence time from 3.2% (mol%) in 1 h to 8.4% in 8 h, as shown in Table A. Apparently, H₂ was produced through dehydrogenation, cyclization and condensation reactions. Free hydrogen atom for the reaction 9 could be formed by the H-abstraction reaction of a radical from molecular H₂. Such radical H-abstraction reactions require relatively low activation energy, e.g., 11.3, 15.2, and 16.0 kcal/mol for CH₃•, C₂H₅• and 1-C₃H₇• respectively [Allara and Shaw, 1980]. When the free hydrogen becomes available, the olefin hydrogenation can proceed easily. This is because such reactions require very low activation energies. The activation energies for hydrogen-atom addition to C₂ to C₅ 1-alkenes to form 2-alkylradical at 700 K are as low as 1.2-1.5 kcal/mol.

Scheme IV. Hydrogenation of 1-alkene products during n-alkane pyrolysis

In regard to other reactions of olefins, it was recently reported that alkylation of the olefin by the radicals can produce C₁₈ to C₃₀ branched alkanes during liquid-phase pyrolysis of n-hexadecane [Ford, 1986]. Such reactions, if any, could also compete with the reactions 9 and 10. The activation energies for the addition of CH₃• and C₂H₅• radicals to propylene at 700 K are about 7.4 and 7.5 kcal/mol, respectively [Allara and Shaw, 1980]. However, detailed GC-MS and GC analyses of products in the present work indicate that essentially all the C₄-C₁₃ alkanes and C₄-C₁₃ alkenes produced from n-C₁₄ under the present conditions are straight-chain products. These results suggest that C₁₅ to C₁₈ n-alkanes detected in this work was due to the combination of two 1-alkyl radicals.

Higher alkanes such as pentadecane, hexadecane, heptadecane, and octadecane were also detected in very small amounts from n-C₁₄ after 6-150 min at 450°C. These products have 1-9 more carbon atoms in their chain than n-C₁₄, indicating the occurrence of radical recombination between two primary radicals C_mH_{2m+1}• and C_nH_{2n+1}• generated from n-C₁₄ (eq.8, Scheme I). These higher alkanes begin to diminish after 1 h at 450°C.

2. Hydrogen-transferring pyrolysis of n-tetradecane. Table B presents the results for hydrogen-transferring pyrolysis of n-tetradecane in the presence of hydrogen donor, tetralin. For H-transferring pyrolysis at 450°C for 30 min, adding tetralin significantly suppressed the decomposition of n-C₁₄. Upon addition of 10 vol% tetralin, the

conversion of n-C₁₄ decreased from 32 to 11 mol % after 21 min, and from 53 to 37 mol% after 30 min. Pyrolysis of n-C₁₄ in the presence of tetralin at 450°C for 12-30 minutes gave decreased yields of both alkanes and alkenes. Surprisingly, it was found that the yields of lower alkanes decreased more than those of corresponding 1-alkenes upon tetralin addition. For example, for n-C₁₄ pyrolysis at 450°C for 30 min, 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.

It is also apparent from Table B that methane formation from n-C₁₄ was suppressed greatly by adding tetralin. The extent of decrease in CH₄ yields, relative to pure n-C₁₄ pyrolysis, increased with increasing amount of tetralin added from 5 to 50 %. At 450°C for 12-30 min with 10 % tetralin, the yields of 1-alkenes from n-C₁₄ also decreased with increasing carbon-number from 4 to 13.

The effects of tetralin appear to be dependent upon the residence time. Within the first 6 min, the effects of tetralin on n-C₁₄ pyrolysis are small. This is primarily because the first 6 min involves mainly the heat-up period, and the extent of decomposition of n-C₁₄ is very small, only 4%. When the residence time is extended to 12 min, the presence of 10 vol% tetralin had a remarkable effect: 12% more n-C₁₄ remained unconverted, in other words, the decomposition of n-C₁₄ was "inhibited" by about 14 % [$(94.6-83.1)/83.1 = 13.8\%$]. The presence of 10 vol% tetralin suppressed the decomposition of n-C₁₄ by about 31 % [$(89.2-68.3)/68.3 = 30.6\%$] after 21 min, and by about 42 % [$(66.2-46.7)/46.7 = 41.8\%$] after 30 min.

We have reported recently that adding tetralin or decalin can significantly suppress solid formation [Song et al., 1992a, 1992d]. 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 V.

Based on the compositional differences of the products and the mechanisms shown in Schemes I and V, it seems that tetralin is more effective in stabilizing the *pri*-radicals than the *sec*-radicals, the latter being more stable than the former. In other words, *pri*-radical appears to be more active than *sec*-radical in abstracting hydrogen from tetralin, and this leads to decreased yields of alkanes and alkenes but with increased ratio of alkene/alkanes for the short duration runs. In long duration pyrolysis, the effect of tetralin

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

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 contribute appear to be the elimination or reduction of solid formation [Song et al., 1992d] and inhibition of the formation of C₁-C₄ hydrocarbon gases, as can be seen from Table B.

References

- 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 Monograph 1, ASTM: Philadelphia, 1991, 163 pp.
- Lai, W.-C.; Song, C.; Schobert, H.H., *Am. Chem. Soc. Div. Petrol. Chem. Prepr.*, 1992d, 37 (4), 1671-1680.
- Poutsma, M.L., *Energy & Fuels*, 1990, 4 (2), 113-131.
- Roquemore, W.M.; Pearce, J.A.; Harrison III, W.E.; Krazinski, J.L., and Vanka, S.P., *Prepr. Pap. - Am. Chem. Soc., Div. Petrol. Chem.*, 1989, 34 (4), 841-849.
- 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, 96 pp.
- 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, 180 pp.
- Song, C.; Eser, S.; Schobert, H.H.; Hatcher, P.G., *Am. Chem. Soc. Div. Petrol. Chem. Prepr.*, 1992a, 37 (2), 540-547.

- Song, C.; Hatcher, P.G., Am. Chem. Soc. Div. Petrol. Chem. Prepr., 1992b, 37 (2), 529-539.
- Song, C.; Peng, Y.; Jiang, H.; Schobert, H.H., Am. Chem. Soc. Div. Petrol. Chem. Prepr., 1992c, 37 (2), 484-492.
- Song, C.; Lai, W.-C.; Schobert, H.H., Am. Chem. Soc. Div. Petrol. Chem. Prepr., 1992d, 37 (4), 1655-1663.
- Song, C.; Eser, S.; Schobert, H.H.; Hatcher, P.G., Energy & Fuels, 1993a, in press.
- Zhou, P.; Hollis, O.L.; Crynes, B.L., Ind. Eng. Chem. Res., 1987, 26, 846-852.

Task 2. Investigation of Incipient Deposition

Growth and Deposition of Particles During Heating of Coal-Derived Aviation Gas Turbine Fuels (Contributed by Peter Walsh and Prashant Sanghani)

Introduction

The objective of the work described in this section is to provide the link between fundamental kinetic studies of changes in fuel composition and the growth of deposits from jet fuels under conditions encountered or anticipated in the fuel systems of gas turbine engines. The emphasis of the work is on the behavior of coal-derived fuels, and the dependence of carbon formation from these fuels on fuel composition, temperature, dissolved oxygen, and the presence of sulfur, metals, and other impurities.

We imagine that the process of deposit formation is intimately connected with the formation of particles in suspension, the suspended particles possibly serving as both a sink for reactive species which might otherwise react to form deposit directly on the wall, and as a source of solid material which deposits by diffusion, inertia, gravitational settling, or filtration. The measurements made in connection with this study therefore include the size and concentration of particles in suspension, in addition to the mass of carbonaceous solid deposited on the wall of the microautoclave reactor.

Measurements

The size distribution of particles suspended in coal-derived jet fuel after 6 hours of heating at 450°C under nitrogen is shown in Figure 15. The size distribution, determined by laser diffraction (Malvern droplet and particle sizer), contains a broad distribution of particles over the range from 3 to 20 μm and a second group of particles having sizes smaller than 2 μm . The presence of both submicron and supermicron

particles in stressed fuels was reported by Klavetter, O'Hern, Marshall, Merrill, and Frye (1990). The larger particles are expected to form by coagulation of the smaller particles, both during and after stressing, since direct addition of reactive species to the larger particles is expected to be slow in the presence of a similar concentration (mass/volume) of particles more than ten times smaller.

Measurements of the dependence of deposit formation on fuel composition were begun by examining the effect of addition of tetradecane to the coal-derived fuel. The results of addition of 5 to 18 wt% tetradecane on deposition and suspended particle concentrations after 6 hours at 450°C in the presence of nitrogen are shown in Figure 16. The mass fraction of the initial charge to the reactor converted to deposit and mass fraction of particles suspended in the liquid were roughly proportional to the mass fraction of paraffin added to the coal-derived fuel, at the low extents of conversion studied.

Discussion

Solid carbonaceous deposits form on all of the inside surfaces of the tubing bomb reactor. Work by other investigators under this research program has shown that the deposit on the bottom of a vertically-oriented reactor is sometimes thicker than the deposit on the vertical walls. The deposit on the vertical walls is pyrolytic, while that on the bottom can contain both pyrolytic carbon and mesophase (S. Eser and C. Song, personal communications, 1992). These observations, and the large sizes of particles present in the distribution shown in Figure 15, suggest that gravitational settling may be an important route for deposition of suspended particles in the tubing bomb. The present measurements of particle size and concentration were used to examine the contribution expected from settling.

The deposition rate, per unit of reactor volume, is the product of the particle concentration, settling velocity, and the ratio of the plan area of the reactor to its volume (equal to the average distance which the particles must travel). A typical concentration of particles in suspension is 1 kg/m³, and the settling velocity of 10 µm particles having a density of 1200 kg/m³ is approximately 1 mm/s. The ratio of plan area to volume is on the order of 100 m⁻¹. The product of these numbers implies a deposition rate of 0.1 kg/m³·s, in contrast with an observed deposition rate, to all walls, averaged over the six-hour duration of the measurements, of approximately 10⁻⁴ kg/m³·s. This comparison suggests that only a small fraction of the suspended particles are in the size range which settles at a significant rate, and that the primary mechanism of deposit formation, in the

present experiments, is diffusive transport of reactive species or small particles through the fluid to the wall.

Reference

E. Klavetter, T. O'Hern, B. Marshall, R. Merrill, and G. Frye, "Advanced Thermally Stable Jet Fuels Development Program Annual Report, Vol. 1 - Model and Experiment System Development, Sandia National Laboratories, Albuquerque, NM, WRDC-TR-90-2079, Vol. 1, September 1990.

Task 3. Characterization of Solid Gums, Sediments, and Carbonaceous Deposits

1. SEM Study of the Deposits on Stainless Steel Flow Reactor Tube Surface (Contributed by Jun Li and Semih Eser).

Discussion

One half of a stainless steel reaction tube (18" in length) deposited with carbon from thermal stressing of a jet fuel was obtained from Sandia National Laboratories. A visual estimation of the color changes along the tube is shown as Figure 17. The semi-cylindrical tube was further cut into 3 x 5 pieces labeled as I 1-5 to III 1-5 along the flow direction. Each piece was examined by SEM to obtain a morphology profile of the deposit along the reactor tube.

Inner surface of the clean reactor tube is rough, looking like extended hills with "buttons" (grains) of different sizes scattered on and in-between the hills. There are also some black spots on the surface. There are mainly three types of deposits: mobile carbon island, carbon mound, and particulate carbon. The particulate carbon can be further divided into three subgroups: coalesced particulate clusters, continuous grown particulate carbon layer, and finely dispersed particulate carbon. The mobile carbon islands have been observed at both ends of the reactor tube. They deposit around the edges of the buttons (metal grain boundaries), and coalesce and move, trying to form an extended network. The growth of this type of deposit is the initial and final stage of the deposition process. Thus it is incomplete and is soon replaced by the dominant growth pattern—particulate growth. It does not grow on the button probably because the edges, as grain boundaries, are more favored sites for deposit growth. Carbon mound is observed at the boundaries of the deposition seen by the naked eye. This type of deposit is not seen at the exit end of the tube. For the particulate carbon, a distinct feature is the formation of

layered deposit structure. Usually, the coalesced particulate clusters are covered by a continuously grown particulate carbon layer. The holes of the top layer are not necessarily correspond to the button. A relevant discussion in the literature (Lahaye and Prado, 1976) suggests that this is probably because of the competition between the formation of surface pyrolytic carbon and the gas-borne carbon. Deposition of pyrolytic carbon on the substrate results in a decrease of surface area, thereby inhibiting further adsorption and growth of the surface carbon. Meanwhile, gradually more finely dispersed carbon is formed in the gas phase. A portion of the carbon becomes adsorbed on the formerly deposited carbon. Consequently, the surface area temporarily increases, and conditions for the formation of a new layer of surface carbon are resumed. In addition, gas-borne carbons are supposedly to take the surface protrusion (here the buttons) as the growth cone (Bokros, 1969). This indicates that the particulate around the button edges must not be formed in the gas phase. Rather, they are probably the surface pyrolytic carbon. As the fuel flows deeply into the tube (i.e., the latter half of the reactor tube), more finely dispersed carbon is formed. This kind of carbon is easy to deposit on the imperfect carbon substrate, thereby filling the holes of the layers to form a continuous grown carbon layer.

Conclusions

Some general conclusions which follow from the analyses of carbon deposits, morphologies on metal grids, and flow reactor deposits are summarized below:

Carbon deposition is related to the transfer properties of the reaction system. The distinct layered structure of deposit and the cycling of light to heavy deposition in different locations on the surface of a flow reactor tube are clues to the competition of different deposit mechanisms, e.g. surface carbon vs. gas-borne carbon formation.

References

- Bokros, J.C. (1969). Chemistry and Physics of Carbon, (P.L. Walker, Jr., ed.), Vol. 5: p.1.
- Lahaye, J. and Prado, G. (1978). "Mechanism of carbon black formation", in Chemistry and Physics of Carbon, (P.L. Walker, Jr., ed.), Vol. 14: p167.

2. Effects of Adding Solid Carbons on Thermal Degradation of Jet Fuel (Contributed by Katia Gergova and Semih Eser).

We conducted earlier thermal stressing of JP-8 jet fuel in the presence of two different activated carbons, carbon black and graphite spectroscopic powder SP-1, at 450°C for 5 hours and at 475°C for 2.5 hours. The presence of solid carbons, especially of activated carbons, during thermal stressing of JP-8 jet fuel and a model compound n-dodecane causes substantial changes in the degradation reactions.

A notable effect of adding activated carbon is the prevention of solid deposition on the metallic reactor surfaces even after rather severe thermal stressing of JP-8 jet fuel, at 450°C for 5 hours. Different microstructures of the deposits observed on the added solid carbons indicated that the deposition mechanisms are also affected by the presence of different carbons during thermal stressing of jet fuel.

Additional thermal stressing experiments were carried out on JP-8 jet fuel in the presence of alumina and carbonaceous deposits produced previously from thermal stressing of JP-8 jet fuel alone. These experiments can provide insights into understanding the role of initial carbonaceous deposits on further formation and deposition of solids during thermal stressing.

We conducted thermal stressing of 10 ml JP-8 jet fuel mixed with 1g alumina and 200 mg carbonaceous deposit. Thermal stressing experiments were carried out at 450°C for 5 hours. The carbonaceous solids were examined by optical microscopy.

Microscopic Examination of Solid Deposits

Figure 18 shows a polarized-light micrograph of the deposit obtained from JP-8 stressed alone and Figures 19 and 20 show the micrographs of the solids from JP-8 mixed with alumina and a previously produced deposit, respectively. All the deposits have anisotropic microstructures. However, the carbonaceous solids formed on the metallic surface have finer grained structures than the solids formed after stressing of JP-8 mixed with alumina and deposit. Apparently, the mechanisms that led to the deposition of these solids are different, as evident in the microstructural differences between the deposits. The deposits collected on the metallic surface (Figure 18) show signs of gas phase nucleation in the form of liquid droplets which collect on metal surfaces and continue carbonization on the surface to form continuous bands of solids.

Figure 19 shows that the solids produced in the presence of alumina are either in the form of long thin particles with a fine texture deposited from the gas phase or larger, isometric particles consisting of large-grain anisotropy formed by primarily liquid phase

carbonization on alumina particles. It is not surprising to see that alumina particles affect solid deposition, because of the presence of acidic sites in alumina which are known to be active in catalyzing cracking reactions.

Figure 20 shows the effect of adding previously formed deposits on solid deposition during thermal stressing of JP-8. One can clearly see the boundary between the added deposit and the newly formed deposit. The pyrolytic carbon microstructures of the newly formed deposits indicate that they are formed by gas-phase deposition processes on the added solids. The observation that all added the solid particles were coated with fresh deposit suggests that the surfaces of the added carbonaceous solids provide attractive areas for further deposition. These results are confirmed by the amount of carbonaceous solids collected on the walls and at the bottom of the reactor after thermal stressing. While solid on the reactor walls after stressing of JP-8 alone is 84 mg, the amounts of solids after thermal stressing of JP-8 mixed with alumina and original deposit were 150 and 218 mg, respectively. It is interesting to note that more solids were formed upon addition of 200 mg of carbonaceous deposits than in the presence of 1 g alumina which contains high concentrations of active sites for catalyzing cracking reactions.

Yield and Composition of Liquid Products from Stressing Experiments

As reported before, the concentration of long-chain paraffins in the liquid obtained from JP-8 mixed with activated carbons was significantly higher than that in the liquid obtained from JP-8 stressed alone at 450°C for 5 h. In order to follow the effect of solid carbon addition as a function of reaction time, shorter duration stressing experiments, i.e., 0.5 and 1 hour, were carried out at 450°C.

Table C shows the yield and composition of all the liquids obtained after stressing of JP-8 jet fuel alone and with different added solid carbons at 450°C for 5 hours. In addition to the yield, Table C presents some compositional parameters, including the ratio of the GC (FID) peak areas of alkanes to aromatics and undecane to naphthalene, and undecane to phenanthrene (or anthracene) to compare the chemical constitution of the liquids obtained after stressing of JP-8 with and without the added solids. The yield of liquids obtained after stressing of jet fuel with the activated carbon at 450°C for 1 hour is 16% lower than the yield of liquid obtained after stressing of JP-8 alone. This difference between the two samples (with and without the carbon) did not change much after 5 hours of stressing (17%). Most probably, the lower liquid yield obtained with the added activated carbon is mainly due to the adsorption of stressed products on active surfaces. Another reason for obtaining lower liquid yields upon adding activated carbons could be

due to the catalysis of recombination reactions on carbon surfaces to produce more gases (Table D). Generally, the addition of solid carbons leads to the production of less C_1 and C_2 and more C_3 , C_4 and C_5 compounds.

Table 5 gives the GC and GC/MS results for the liquid obtained after stressing of JP-8 alone and with activated carbon at 450°C for 0.5 and 1 hour. For comparison, the identified compounds and the respective GC peak areas for the JP-8 neat are also given in Table 5. The results show that the short-chain alkanes, not present in original the JP-8 neat are produced by cracking reactions during thermal stressing. In general, the concentration of short-chain alkanes is higher in the samples obtained from thermal stressing of JP-8 alone. It should be noted that the concentration of alkenes and cycloalkanes in the liquid obtained after stressing of JP-8 with activated carbon is higher or at least the same as that in the liquids obtained from the thermal stressing of JP-8 alone. Further, a comparison of the percent distribution of peak areas obtained from the GC data indicate that the concentration of long-chain paraffins starting from carbon number 9 is higher for the liquid obtained from the stressing of JP-8 mixed with the activated carbon.

Figures 21a and 21b show the gas chromatograms of the liquid obtained after stressing JP-8 alone and with the activated carbon at 450°C for 1 hour. These chromatograms clearly show the higher concentrations of long-chain alkanes in the liquids produced in the presence of the activated carbon. These results confirmed our earlier observations that the activated carbon surface appears to be effective in stabilizing the free radicals and preserve constituent paraffins in the jet fuel at 450°C.

A series of plots were prepared to compare the relative concentrations of selected compounds in the liquids obtained after stressing of JP-8 jet fuel at 450°C with and without the added activated carbon.

Figure 22 shows the alkane carbon number as a function of percent peak area obtained by GC for the liquids stressed with and without activated carbon at 450°C for 1 hour. The same parameters for the JP8 neat are plotted for comparison.

The concentration of the alkanes with fewer than seven carbon atoms for the jet fuel stressed alone is higher than for the JP-8 stressed with activated carbon. With the increasing alkane carbon number, on the contrary, the concentration is higher for the liquid obtained after thermal stressing of JP-8 with activated carbon. As shown in Figure 22, the original jet fuel has a high concentration of n-C-10 and n-C-11 alkanes, which is an indication that activated carbon addition leads to preservation of the compounds present in the initial fuel sample.

Table 5. Compounds identified and percent peak areas of the JP-8 neat and the liquids obtained after thermal stressing of JP-8 alone and in the presence of the activated carbon.

COMPOUNDS	Area %				
	JP-8 450°C 1 h	JP-8 +AC 450°C 1 h	JP-8 450°C 0.5 h	JP-8 +AC 450°C 0.5 h	JP-8 neat
N-BUTANE+ BUTENE	4.16	0.46	1.12	0.37	
2-METHYLBUTANE	1.93	1.07	0.7		
N-PENTANE	3.71	1.99	1.3	1.92	
PENTENE	0.88	0.53	0.34	0.04	
PENTENE+METHYLPENTANE	1.2	1.01	0.68	0.26	
3-METHYLPENTANE+METHYL- CYCLOPENTANE	0.56	0.79			
N-HEXANE	2.18	1.75	0.78	0.8	
CYCLOHEXANE	0.84	0.36		0.23	
HEXENE	0.83	0.33	0.22	0.18	
METHYLHEXANE+METHYL- CYCLOPENTANE	1.1	1.12	0.42	0.61	
3-METHYLHEXANE	0.65	0.4	0.17	0.34	
N-HEPTANE	1.6	1.74	0.82	0.99	
DIMETHYLCYCLOPENTANE	1.33	1.04	0.76	0.65	
HEPTENE	0.18	0.5	0.12	0.1	
METHYLCYCLOHEXENE	0.21	0.2	0.15	0.13	
CYCLOHEXENE+BR ALKANE	1.28	2.1	0.91	1.14	
C2-CYCLOPENTANE+BENZENE	0.44	0.86	0.46	0.52	
N-OCTANE	1.66	2.55	1.36	1.23	
METHYLCYCLOHEXENE	1	0.6	0.66	0.42	
4-METHYLOCTANE	0.57	0.83	0.37	0.65	
DIMETHYLCYCLOHEXANE	0.46	0.45	0.3	0.31	
DIMETHYLCYCLOHEXANE	0.4	0.26	0.18	0.15	
ALKYLCYCLOHEXANE	1.75	1.27	1.28	1.4	
B ₂ ALKANE	1.15	1.15	0.94	0.93	
TOLUENE	1.16	0.88	0.37	0.37	
N-NONANE	2.19	2.63	2.05	0.21	0.99
C3-CYCLOHEXANE	0.84	0.98		0.78	
5-METHYLNONANE	0.61	0.62	0.72	0.76	
C3-CYCLOHEXANE	0.7	0.67	0.69	0.66	
4/2-METHYLNONANE	1.04	1.2	1.23	1.31	1.25
N-PROPYLCYCLOHEXANE	0.44	0.52	0.5	0.49	0.35
3-METHYLNONANE	0.56	0.65	0.64	0.66	0.6
ETHYLBENZENE	1.93	2.4	1.25	1.37	0.33
C4-CYCLOHEXANE	0.23	0.27	0.3	0.3	0.29
N-DECANE	2.94	3.3	3.45	3.57	3.75
C4-CYCLOHEXANE	0.85	0.89	0.95	0.97	0.6
DIMETHYLBENZENE+DIMETHYL- NONANE	1.46	1.55	1.92	1.63	1.46

COMPOUNDS	Area %				
	JP-8 450°C 1 h	JP-8 +AC 450°C 1 h	JP-8 450°C 0.5 h	JP-8 +AC 450°C 0.5 h	JP-8 neat
C4-CYCLOHEXANE	0.3	0.31	0.49	0.49	
5-METHYLDECANE	0.27	0.27	0.44	0.63	0.78
4+2-METHYLDECANE	0.42	0.41	0.61	1.3	1.77
N-BUTYLCYCLOHEXANE+ C3-BENZENE	0.9	0.89		1.16	0.19
3-METHYLDECANE	0.91		0.91	0.68	0.84
C3-BENZENE(ISOMERS)	1.74	2.14	0.7	1.56	0.93
N-UNDECANE	3.7	4.1	4.77	4.94	0.19
C3-BENZENE	1.19	0.88	0.68	0.71	0.5
UNDECENE	0.47	0.42	0.6	0.58	
TRIMETHYLBENZENE	2.11	2.17	1.79	1.77	1.22
DECALIN	0.75	0.78	0.97	0.96	0.83
BR ALKANE+ALKYLCYCLOHEXANE	0.42	0.43	0.56	0.49	0.49
ETHYLDIMETHYLBENZENE	0.71	0.85	0.77	0.78	0.74
6-METHYLUNDECANE	0.29	0.31	0.43	0.41	0.57
C3-BENZENE	0.35	0.34	0.49	0.53	0.88
4-METHYLUNDECANE	0.95	1.12	1.05	1.07	1.28
2-METHYLUNDECANE			0.74		1.1
METHYLDECALIN	0.51	0.57		0.76	0.17
METHYLPROPYLBENZENE	1.15	1.14	1.24	1.09	1.33
METHYLPROPYLBENZENE	0.59	0.69	0.8	0.79	1.11
N-C5 CYCLOHEXANE+N-C4 BENZENE+BR ALKANE	0.81	0.91	0.91	0.92	1.16
C4-BENZENE	0.56	0.71	0.49	0.49	0.48
METHYLPROPYLBENZENE+INDAN	0.72	0.59	1.04	0.77	
N- DODECANE+TETRAMETHYLBENZENE	2.74	3.19	4.32	4.04	5.23
2,6-DIMETHYLUNDECANE	1.25	0.58	1.16	1.22	2.35
C6-CYCLOHEXANE	0.64		0.45	0.46	
C4-BENZENE	0.91	1.05	0.64	0.72	1.04
C5-BENZENE	0.39	0.42	0.54	0.57	
C2-DECALIN	0.32	0.37	0.6	0.35	0.3
C4-BENZENE	0.19	0.2	0.49	0.26	0.62
METHYLINDAN	0.5	0.51		0.59	
C4-BENZENE(ISOMERS)	0.46	0.5	0.44	0.51	
C4-BENZENE	0.39	0.38	0.38	0.45	0.28
5-METHYLDODECANE	0.26	0.25	0.4	0.32	0.61
BR ALKANE	0.79	0.8	1.04	1.11	1.44
C4-BENZENE	0.24	0.5	0.51	0.42	0.49
2,6-DIMETHYLUNDECANE+C5-BENZENE	1.05	1.3	1.55	1.63	2.41
C5-BENZENE					0.19
3-METHYLDODECANE+C5-BENZENE	0.82	1.21	1.07	1.46	1.49
N-HEXYLCYCLOHEXANE	0.65	0.54	0.79	0.71	0.74

COMPOUNDS	Area %				
	JP-8 450°C 1 h	JP-8 +AC 450°C 1 h	JP-8 450°C 0.5 h	JP-8 +AC 450°C 0.5 h	JP-8 neat
C5-BENZENE	0.29	0.2	0.4	0.34	
C5-BENZENE	0.2	0.13	0.24	0.17	0.24
C5-BENZENE	0.19	0.16	0.26	0.24	0.23
C4-BENZENE	0.29	0.19	0.37	0.35	0.31
N-TRIDECANE+C5-BENZENE	2.44	2.16	4.03	3.98	5.28
METHYLINDAN + BR ALKANE	0.5	0.3	0.64	0.76	0.95
METHYLINDAN+TETRALIN+C5-BENZENE			0.45	0.82	0.68
BR ALKANE	0.17	0.23	0.4	0.38	0.66
C5-BENZENE	0.18	0.26	0.49	0.33	1.21
METHYLINDAN			0.32		0.55
BR ALKANE	0.31	0.27	0.49	0.59	0.79
BR ALKANE	0.36	0.57	0.53	0.72	1.07
BR ALKANE+ALKYLBENZENE	0.36	0.38	0.67	0.73	1.39
BR ALKANE	0.21	0.26	0.34	0.43	0.71
ALKYLBENZENE			0.06	0.11	
C6-BENZENE+METHYLTETRALIN	0.13	0.17	0.71	0.56	0.51
N-HEPTYLCYCLOHEXANE	0.37	0.17			0.68
BR ALKANE	0.06			0.07	0.35
N-TETRADECANE	1.1	1.23	1.83	1.8	3.15
NAPHTHALENE	0.65	0.92	0.52	0.6	
C2-INDAN	0.07	0.19	0.05	0.19	
C5-BENZENE		0.1	0.11	0.14	
METHYLTETRALIN+BR ALKANE	0.15	0.06	0.64	0.61	
4-METHYLTETRADECANE+DIMETHYL-INDAN	0.45	0.21		0.37	
BR ALKANE+METHYLINDENE	0.28	0.28		0.23	
BR ALKANE	0.15	0.17		0.22	
BR ALKANE	0.14	0.17		0.07	
METHYLTETRALIN	0.3	0.19	0.43	0.04	0.37
N-PENTADECANE	0.8	0.99	1.43	1.4	2.14
2-METHYLNAPHTHALENE	0.9	1.43	0.79	1	1.85
1-METHYLNAPHTHALENE	0.58	1.05	0.48	0.79	0.76
BR ALKANE	0.03	0.03		0.13	0.15
BR ALKANE	0.03				0.13
BR ALKANE	0.05	0.05			
N-HEXADECANE	0.31	0.28	0.43	0.4	0.58
2-ETHYLNAPHTHALENE	0.15	0.25	0.16	0.17	
DIMETHYLNAPHTHALENE	0.18	0.28	0.2	0.2	
DIMETHYLNAPHTHALENE	0.19	0.3	0.21	0.24	0.16
BIPHENYL	0.08	0.14	0.09	0.09	0.11
DIMETHYLNAPHTHALENE	0.06	0.15	0.15	0.11	0.18
DIMETHYLNAPHTHALENE	0.23	0.33	0.2	0.23	0.18

COMPOUNDS	Area %				
	JP-8 450°C 1 h	JP-8 +AC 450°C 1 h	JP-8 450°C 0.5 h	JP-8 +AC 450°C 0.5 h	JP-8 neat
DIMETHYLNAPHTHALENE	0.51	0.76	0.44	0.53	0.48
DIMETHYLNAPHTHALENE	0.12	0.18	0.14	0.15	0.13
DIMETHYLNAPHTHALENE	0.05	0.08	0.06	0.06	0.04
METHYLBIPHENYL			0.1	0.09	
N-HEPTADECANE	0.17	0.22	0.12	0.13	0.22
DIMETHYLNAPHTHALENE	0.07	0.1	0.05	0.07	0.08
DIMETHYLNAPHTHALENE	0.06	0.1	0.05	0.06	0.05
METHYLBIPHENYL	0.07	0.12	0.07	0.08	0.06
C3-NAPHTHALENE	0.09	0.15	0.09	0.1	0.08
C3-NAPHTHALENE	0.25	0.35	0.24	0.26	0.25
C3-NAPHTHALENE	0.07	0.12	0.08	0.07	0.08
C3-NAPHTHALENE	0.06	0.1	0.08	0.07	
C3-NAPHTHALENE	0.09	0.13	0.1	0.09	0.09
C3-NAPHTHALENE+ALKANE	0.05	0.09	0.06	0.05	0.03

Figure 23 shows the alkane carbon number as a function of the product yield for the liquid obtained with and without the activated carbon at 450°C for 1 hour. The relative liquid product yields were calculated by multiplying the respective percent peak area by the yield of liquid products. Generally, all the alkanes show higher product yields for the liquid obtained after stressing of JP-8 without carbon. These results are expected considering that activated carbon adsorbed a considerable part of the liquid (its weight doubled after the thermal stressing).

In Figure 24, the alkane carbon number is plotted against the ratio obtained from the percent area of particular alkane and an aromatic molecule eluting next to the alkane for the liquid obtained after stressing of JP-8 alone and with activated carbon at 450°C for 1 hour and 0.5 hour. For both reaction times, 1 hour and 0.5 hour the ratio of alkane/aromatic compounds appears to be higher for the liquid obtained after thermal stressing of JP-8 mixed with the activated carbon. These data confirmed previously reported results for the 5 hours reaction time, which showed that the liquid obtained after stressing of jet fuel with carbon has higher concentration of alkanes and lower concentration of alkylbenzenes compared to the liquid obtained from the JP-8 alone. It should be noted that the measurable thermal degradation begins within the first half hour of the thermal stressing of jet fuel at 450°C.

The n-tetradecane to naphthalene, n-pentadecane to methyl naphthalene and n-hexadecane to dimethyl naphthalene ratios for both liquids with and without activated

carbon at 450°C for 1 hour and 0.5 hour are shown in the Figure 25. In contrast to the alkane/alkylbenzene ratios, in this case, the concentration of naphthalenes is higher for the sample obtained after thermal stressing of JP-8 with activated carbon. Because of the relatively lower concentration of naphthalenes in the liquids, the very small difference in the relative amount of these compounds are translated into large differences among the plotted ratios. One should note that the concentration of methyl and dimethyl naphthalene in the original jet fuel is almost the same as that in the liquid obtained after stressing of jet fuel with the activated carbon. Most probably naphthalenes are not critically important for the stability of jet fuel during thermal stressing at 450°C or at least not in these low concentrations, as was also shown by our previous data.

In Figure 26 and 27 the number of alkyl groups on benzene are plotted against the percent peak areas for the JP-8 neat, JP-8 stressed alone and with activated carbon at 450°C for 0.5 h and 1 hour respectively. With the increasing number of alkyl groups, the percent area increases for the original JP-8 jet fuel. The JP-8 neat does not have any toluene.

The percent area of the peaks for both liquids with and without the activated carbon for both reaction periods increase with the increasing number of methyl groups on benzene up to three methyl groups after which they decrease (i.e., for benzene with four methyl groups). The decrease is sharper for the one hour reaction time. It should be noted that there is no significant difference between the liquids obtained from stressing of JP-8 alone and mixed with the activated carbon.. Generally, the sample obtained from the jet fuel stressed with carbon have higher concentration of alkylbenzenes, especially two and three methyl groups on benzene for one hour reaction period. Evidently, the addition of activated carbon does not affect very much the concentration of the alkylbenzenes or at least not as much as the concentration of the long-chain paraffins.

It is clear that the addition of different solid carbons during thermal stressing of JP-8 jet fuel leads to different reaction mechanisms. Some of the added carbons (activated carbon, carbon black and graphite) prevent the solid deposition during thermal stressing of JP-8 at 450°C for 5 hours. The other solids used in this study, alumina and deposit obtained from stressing of jet fuel, evidently, provide more attractive areas for carbon deposition than stainless steel reactor surfaces. As a result, a considerable increase in the amount of carbonaceous solid was seen upon addition of alumina and the previously produced deposit. Considering that the acidic sites in alumina act as strong centers for catalyzing cracking reactions, it is interesting to note the presence of previously produced solid deposits can produce more solids than alumina. The presence

of different solid carbons affects also the deposit mechanism and the microstructure of the carbonaceous solids.

In future studies, the effects of the surface area and pore size distribution of activated carbons on solid deposition will be investigated, as well as the behavior of other jet fuel samples (e.g., Jet A-1 and JPTS) in the presence of different solid carbons.

Task 4. Coal-based Fuel Stabilization Studies

1. Use of ^{13}C Labels To Trace Reactions of Potential Antioxidants for Jet Fuels (Contributed by Daniel McKinney, Jacqueline Bortiatynski, and Patrick Hatcher).

Introduction

Addition of antioxidants to retard cracking of the complex assemblage of hydrocarbons comprising jet fuels is a strategy being examined to prevent or delay the formation of solid deposits. Coleman et al. have demonstrated that benzyl alcohol and 1,4-benzenedimethanol are effective additives for the retardation of solid-deposit formation in jet fuel subjected to a temperature of 425 °C^{1,2}. They have attempted to provide mechanistic details to explain the effect of the additives; however, the techniques employed, infrared spectroscopy¹, ^1H NMR², and gas chromatography/mass spectrometry have been only able to partially identify reaction mechanisms due primarily to the fact that the complexity of the jet fuel components obscures the various reaction intermediates. The inability to quantitatively differentiate all the reaction intermediates from compounds present in the jet fuels prior to thermal stressing limits the ability to assess reaction mechanisms.

From other studies (not a part of the Jet Fuel project) involving examination of the reactivity of pollutants such as 2,4-dichlorophenol with complex macromolecules such as humic substances, we have developed expertise in the use of ^{13}C -labeled compounds to examine the reactivity of specific compounds in complex mixtures³. Reactions involving the ^{13}C -labeled carbon lead to significant changes in the chemical shift of this carbon in ^{13}C NMR spectra. By enriching the reactive compound with 100% ^{13}C at the one reactive site, an enhancement in the ^{13}C NMR sensitivity is realized for the labeled carbon. Other unlabeled carbons in the reactive molecule and the reacting substrate are reduced to near background levels in the spectra. Thus, reactions at the labeled site can clearly be discerned by intense NMR signals and differentiated from reactions of the unlabeled carbons which are either not observed or observed at much reduced levels compared to labeled carbons.

With this same approach, we anticipated that many of the thermal reactions of specific compounds or additives in jet fuels could be investigated. We have examined the reactivity of the benzyl alcohol additive with thermally stressed jet fuel in experiments identical to those described by Coleman et al.^{1,2} We used benzyl alcohol labeled with 100% ^{13}C at the (α) benzylic carbon. Any reactions involving this benzylic carbon can be clearly differentiated with ^{13}C NMR.

Experimental

The ^{13}C NMR spectra were obtained on a Bruker WM 360 NMR spectrometer with a resonance frequency of 90.56 MHz. An inverse-gated pulse sequence with a 10 second delay between pulses, and a 45° pulse angle was utilized to ensure the acquisition of quantitative spectral data. The spectral width used in these experiments was approximately 21 kHz, and 96 scans were collected for each experiment. The spectra were transformed using 1 Hz line broadening. The intense peaks in the spectra which result from the ^{13}C labeled carbons were identified using standard chemical shift tables⁴. The relative amount of each product present in the reaction mixture was obtained from the peak height of the ^{13}C labeled carbon.

Mass spectral data were obtained on a Hewlett Packard 5971A Gas Chromatograph / Mass Spectrometer. A J & W Scientific fused silica capillary column (DB-17, 0.25mm i.d. x 30 m) was used for GC separation. A 1 μL sample of the thermally stressed jet fuel -benzyl alcohol mixture was diluted with 1 mL of pentane. An aliquot of this mixture was injected onto a split/splitless injector operating in the splitless mode. The column temperature was programmed from 40°C to 280°C at a heating rate of $4^\circ\text{C}/\text{min.}$, after a 5 minute isothermal period. The ionization mode on the mass spectrometer was electron impact (EI, 70 eV).

Samples for this study were prepared from an essentially additive free Jet A-1 fuel supplied by the Air Force/ WRDC Aero Propulsion Laboratory (No. 90-POSF-2747). Benzyl alcohol labeled in the α position and unlabeled benzyl alcohol were purchased from Aldrich Chemical Company, Milwaukee, Wisconsin and used without further purification. The thermal stressing and sample preparations were carried out in similar fashion as discussed by Coleman, et al.¹ with the following exceptions: 100% labeled α - ^{13}C -benzyl alcohol was mixed with 0.25 mL of unlabeled benzyl alcohol and the mixture was added to 9.5 mL of jet fuel sample. After each stressing period (3 hrs., 6 hrs., 12 hrs.), a 0.5 mL aliquot was removed and placed along with 0.5 mL of deuterated chloroform in an NMR tube and sealed. The reactor was resealed, repressurized and reacted further until the next allotted time. The original process as described by

Coleman, et al.¹ was altered slightly in order to conserve the expensive ¹³C-labeled benzyl alcohol. Otherwise, larger volumes of the labeled material would have been needed in order to carry out a separate experiment for each thermal stressing period.

Results and Discussion

The physical and partial chemical effects due to the thermal stressing of Jet A-1 fuel have been described in a previous report by Coleman et al.¹ The fuel behaved identically to that described in this previous report in that addition of 5% benzyl alcohol delayed formation of carbonaceous residues for periods of up to 6 hours. Fourier transform infrared (FTIR) spectroscopy¹, and ¹H NMR spectroscopy², indicated that a delay of carbonization reactions is linked to the thermal degradation of benzyl alcohol.

Addition of α -labeled benzyl alcohol to Jet A-1 fuel provides a ¹³C NMR spectrum (Figure 28) dominated by the peak of the labeled α carbon at 65.3 ppm. Other peaks in the spectrum are those natural abundance carbons in the jet fuel due to hydrocarbons and the unlabeled carbons of the benzyl alcohol. The relative intensity of the labeled α carbon is 71.4% of the total intensity of all peaks (Table 6).

As the jet fuel/benzyl alcohol mixture is thermally stressed at 425 °C for varying periods of time, the ¹³C NMR spectra change dramatically (Figure 28). The peak for the labeled α carbon of benzyl alcohol gradually diminishes over a period of 6 hours and eventually disappears after 12 hours of thermal stressing. During this period, other sharp peaks evolve. A peak at 21.4 ppm emerges and becomes the major peak in the NMR spectrum of jet fuel stressed for 12 hours. This peak is that of the methyl carbon in toluene, which is derived from the α carbon of benzyl alcohol. Other peaks observed in the thermally stressed fuel are those of the aldehyde carbon of benzaldehyde at 192 ppm, the carboxyl carbon of benzoic acid at 170 ppm, and the ring carbons of benzene at 128.35 ppm. The peaks for toluene, benzaldehyde and benzoic acid represent the ¹³C-labeled carbons of these compounds, but the peak at 128.35 ppm is due to naturally abundant ¹³C in benzene.

Even though previous studies have shown that thermal stressing of jet fuel for the time periods used in our study leads to significant alteration of the fuel-derived hydrocarbons, we do not observe a significant change in the relative distribution of the unlabeled peaks assigned to jet fuel hydrocarbons over the course of 12 hours. We also do not observe the evolution of olefins which would give peaks in the range of 90-140 ppm, in contrast to the observations made by Coleman et al.¹ It may be that the FTIR method used by Coleman et al.¹ is more sensitive to olefin production than the NMR method.

Based on the previous studies by Coleman et al.^{1,2}, it should come as no surprise that benzyl alcohol is thermally degraded to benzaldehyde and subsequently oxidized to benzoic acid. Both of these products were observed by FTIR. Toluene and benzene, however, were not detected in these previous studies due to the inability to distinguish benzyl-alcohol-derived toluene and benzene from the toluene and benzene naturally present in jet fuel, pointing to the value of the NMR approach. The formation of toluene is indicative of C–O bond scission followed by hydrogen abstraction. Benzene is unexpected to provide such an intense peak, considering that it is not expected to contain any of the label. The six aromatic carbons in benzene are present at natural abundance levels, which indicates that at these levels they constitute a major reaction product in the jet fuel. It is likely that the benzene is derived from decarboxylation of benzoic acid, a reaction known to occur under the thermal conditions employed.

Some of the intensity at 128.35 ppm may also be due to one of the unlabeled carbons of toluene. Gas chromatographic and mass spectrometric analysis of the thermally stressed mixture indicates the presence of toluene. The mass spectrum of the toluene (Figure 29) indicates that a significant amount of unlabeled toluene is present. Labeled toluene accounts for 52% of the mass spectrum with major peaks at m/z 93 and 92. It is obvious that this labeled toluene originates from the benzyl alcohol. The presence of a large peak at m/z 91 indicates the presence of unlabeled toluene derived from the unlabeled benzyl alcohol plus perhaps a small fraction derived from the thermally stressed jet fuel.

Perhaps the most significant advantage ^{13}C NMR and use of labels have over other techniques is the ability to quantify the reaction products to trace reaction mechanisms. Furthermore, the tracking of the label can be made quantitatively in the presence of complex mixtures of materials containing natural abundance carbons. Table 6 shows the yield of peaks assigned to specific carbons of individual compounds normalized to the total intensity of peaks in the NMR spectra for each aliquot taken over the course of time during the reaction. This table demonstrates the loss and growth of both labeled and unlabeled carbons. Peak intensities for the specific carbons, both labeled and unlabeled, are normalized to the sum of the intensities of all peaks in the spectra. While we can track the eventual fate of the labeled carbons and assume that this tracks the fate of the compounds associated with the label, loss of the labeled carbon from a product during the thermal heating takes that product out of our sensitivity window. Because the unlabeled carbons on this transformation product are at natural abundance, they will appear in the NMR spectrum at an intensity commensurate with their contribution to the concentration of carbon from all compounds in the mixture. The

steady loss of benzyl alcohol, a trend first described by Coleman et al.^{1,2}, is accompanied by a rise in toluene as the next most abundant product. Benzaldehyde increases during thermal stressing, but the amount of benzaldehyde is not as significant as the toluene. After six hours of heating, the benzaldehyde concentration decreases while the concentration of both benzene and benzoic acid increase slightly.

The way in which the NMR data are presented in Table 6, normalized to total peak intensity, is greatly affected if the labeled carbons are eventually lost by conversion to a gaseous product as in the case of the decarboxylation of benzoic acid. We did not attempt to recover and analyze the carbon dioxide thus formed, and the loss of label can only be determined by difference after accounting for the label from identified labeled products. It is also possible that some of the labeled carbons were incorporated into solid deposits and would not be detected by the NMR method. Summing the intensity of the labeled carbons (Table 6) provides a measure of the relative loss of ^{13}C from the liquid products. Approximately 45% of the label is lost from liquid products over the course of 12 hours of thermal stress. If we assume that this loss is mostly associated with decarboxylation of benzoic acid, then we can estimate that a significant fraction of the peak for benzene (2.3 out of 6.6%) originates from this process. The remainder can be attributed to overlap of one of the peaks for toluene and benzene produced from jet fuel hydrocarbons by thermal stress.

Conclusions

A complex mixture like jet fuel constrains the use of conventional analytical methods for the examination of the role that benzyl alcohol plays in retarding the formation of solid deposits during thermal stressing. ^{13}C -labeling in combination with a standard ^{13}C NMR experiment has been shown to be an excellent means to identify and quantify the products that are formed during this thermally induced process. With the use of the ^{13}C -labeling, products formed as a result of thermal alteration of benzyl alcohol were quantified by following the α - ^{13}C -labeled carbon over the given time intervals for thermal stressing. The distribution of all the identified labeled and unlabeled reaction products indicates that thermal stressing of benzyl alcohol in the presence of jet fuel leads to the production of toluene and benzene as the major species, which were not detected by the methods employed by Coleman et al.^{1,2}, with intermediates being benzaldehyde and benzoic acid. The detailed mechanisms responsible for the production of these compounds and the reasons for retardation of solid deposit formations are not yet clear but is the subject of ongoing research. However, it is clear that by use of labeled substrates in complex systems such as jet fuels one can trace products formed without

Table 6. Intensity of ^{13}C NMR data of specific carbons normalized to the total peak intensity of the spectrum over each allotted time period in minutes.

time, min	α -carbon of benzyl alcohol (65.3 ppm)	α -carbon of benzaldehyde (192 ppm)	α -carbon of toluene (21.4 ppm)	α -carbon of benzoic acid (170 ppm)	benzene (128.35 ppm)	Σ label
0	71.4	0.0	0.0	0.0	0.0	71.4
10	62.0	1.3	4.2	0.0	0.2	67.5
60	44.5	4.0	8.8	0.0	0.7	57.3
180	26.1	6.8	17.3	0.6	1.9	50.8
360	6.1	4.4	31.7	1.3	5.4	43.5
720	0.0	0.0	38.5	1.0	6.6	39.5

interference from other unlabeled portions of the fuel, a major first step in determining the influence of a reacting species such as benzyl alcohol and the mechanism by which retardation of thermal degradation occurs. Perhaps with the combination of FTIR methods plus standard ^{13}C NMR experiments, suitable reaction mechanisms plus reaction products identification can be accomplished.

References:

1. Coleman, M. M.; Selvaraj, L.; Sobkowiak, M.; Yoon, E. *Energy and Fuels* **1992**, *6*, 535-539.
2. Coleman, M. M.; Selvaraj, L.; Sobkowiak, M.; Yoon, E. *Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem.* **1992**, *37* (4), 1664-1670.
3. Bortiatynski, J.M.; Hatcher, P.G.; Minard, R.D.; Dec, J. and Bollag J.M. *6th International Meeting of the International Humic Substances Society Abstracts*, **1992**, 293.
4. Breitmaier, E.; Voelter, W. "*Carbon-13 NMR Spectroscopy: high resolution methods and applications in organic chemistry and biochemistry*"; VCH Publishers: New York, 1987.

2. The Mechanism of Hydrogen Transfer from Hydroaromatic Compounds—A Literature Review (Contributed by Emily Yoon)

Introduction

Our interest in the mechanism of hydrogen transfer from hydroaromatic compounds derives from the potential of using this hydrogen transfer to stabilize jet fuels during thermal stressing. We have discussed some of this work in the current report, under Task 1. Much of the recent literature on hydrogen transfer from hydroaromatics derives from coal liquefaction studies, so the material reported here has a strong liquefaction "flavor" and is also relevant to Task 5 of this project.

Coal liquefaction depends critically on a supply of hydrogen atoms proportionate with the rate of free-radical formation, which is a function of coal structure and reaction temperature. The bridges linking the cyclical units of coals are ruptured when heated to 400–450°C. Bond rupture forms free radicals, which can be stabilized by the addition of a hydrogen atom. If hydrogen capture does not occur, the radicals combine to form stable, and high molecular mass products. One of the hydrogen sources is the liquefaction solvent. The liquefaction solvent not only provides a transport medium for the coal and facilitates heat transfer, but also serves as an important source of transferable hydrogen, and it disperses the liquefaction products¹. This hydrogen-donor solvent serves as a hydrogen source and transfer agent for the degrading coal, and it inhibits the retrograde reactions that lead to solid, unreactive carbonaceous residue.

Hydrogen-donor solvents are known to donate hydrogen to the coal liquefaction system without having to add external hydrogen gas to the system². The value of hydrogen-donor solvents has long been recognized, and their activity is related to the degree of saturation and to the number of condensed rings^{3,4}. The degree of saturation is related to the degree of hydrogenation on multiaromatic ring systems. The most effective hydrogen-donor compounds are those with a partially hydrogenated aromatic structure^{2,3,5,6}—such as tetrahydronaphthalene (tetralin), dihydropyrene, and 9,10-dihydrophenanthrene. The hydroaromatic hydrogens are easily abstracted, leading to stable aromatic compounds and stabilizing the coal free radicals⁷. Neither the parent aromatic compound nor the fully hydrogenated derivative is a good hydrogen donor⁸.

In line with the application of hydroaromatics in coal liquefaction, there are other various uses. Hydroaromatics such as tetralin and octahydrophenanthrene play the role of inhibitor in the autoxidation of hydrocarbons and effectively suppress the formation of colored and high molecular weight products⁹. The inhibiting abilities of heavy

hydroaromatics from petroleum were applied to rubbers and plastics¹⁰. The application of hydroaromatics in thermal stability of aviation jet fuels is on-going research^{11,12}.

Free Radical Hypothesis: Bond-scission/radical-capping mechanism

The free radical hypothesis is the foundation upon which much of the modern interpretation of solvent effects rests. Free radical mechanism is defined as the coal being dissociated by thermal decomposition into free radicals that are stabilized by capture of a hydrogen atom from a donor molecule.² The relevant modes of bond breaking are (1) homolysis of a covalent bond to produce two radicals and (2) β -scission of a radical to produce an unsaturated molecule and a smaller radical. Curran et. al³ proposed a five-step reaction that still forms the framework for much discussion of the mechanism of liquefaction:

These reactions embody the postulate that the rate-controlling step is the homolytic cleavage of carbon-carbon bonds in the coal molecules, which generates two free radicals ($\text{R}\cdot$). These radicals may then abstract hydrogen from donor solvent (DH_2) or coal or the free radicals produced by either of these steps. The net result is the stabilization of the fragments originating from the ruptured bond and dehydrogenation of the solvent.

Liquefaction yields generally increase when good hydrogen donors are present and when their concentration is increased. The coal conversion appears to be little affected by the composition of the solvent and is determined primarily by the amount of hydrogen transfer as shown Figure 30 and Figure 31³.

The study of the rapid pyrolysis of coal in the cavity of EPR spectrometers^{13,14} shows the evidence for the involvement of free radicals. In the study of the thermal decomposition of a bituminous coal by Sprecher and Retcofsky¹⁴, the concentration of radicals increased by a factor of four in about 5 min. at 470 °C. While the addition of 9,10 -dihydrophenanthrene to the reaction mixture inhibited the formation of radicals, the addition of phenanthrene had no effect on the radical concentration. These results support the idea that coal molecules decompose by homolytic reactions to yield transient reactive radicals.

The hydrogen-atom-abstraction reactions occur rapidly with effective donor molecules such as 9,10-dihydrophenanthrene

As shown above, a new coal molecule is produced together with a mobile radical. Hydrogen transfer may proceed through $H\cdot$ as a discrete intermediate, but more commonly, the hydrogen atom is transferred directly from a donor to an acceptor. Since each can be either a spin-paired molecule or a radical, four categories result¹⁶.

- 1) Hydrogen abstraction: a molecular donor and a radical acceptor
- 2) Radical disproportionation: radicals as both donor and acceptor
- 3) Radical hydrogen transfer: a radical donates a β -hydrogen to an unsaturated acceptor
- 4) Molecular disproportionation: both donor and acceptor are spin-paired molecules.

The donor solvent molecules such as tetralin and 9,10-dihydrophenanthrene, then can easily be oxidized to aromatic compounds¹⁵.

The abstraction reactions of the dihydronaphthalenes are more rapid than the abstraction reactions of tetralin. The removals of hydrogen atoms from the intermediate radicals by reactions with other coal radicals are also very rapid processes.

Bockrath and co-workers¹⁷ compared the hydrogen donor abilities of various hydroaromatics toward benzyl radical at 170 °C. Their results lead to a reactivity order

for hydrogen abstraction of 9,10-dihydroanthracene $\gg$ 1,2-dihydronaphthalene $>$ 4,5-dihydropyrene $>$ 9,10-dihydrophenanthrene $>$ tetralin. However, this order does not coincide with the order of effectiveness of these common hydroaromatics when used as model donor solvents in coal liquefaction studies. Thus, in addition to capping radicals to prevent condensation, they must be involved in other functions such as hydrogen-transfer-induced bond breaking and transfer hydrogenation¹⁶.

Concerted Pericyclic Mechanism

According to the free-radical mechanism, donor effectiveness is related to the availability of abstractable hydrogen atoms, and this notion seems to have won general acceptance in the literature because it rationalizes the effectiveness of tetralin, which possesses benzylic hydrogen atoms, relative to naphthalene and decalin, which do not. However, the foregoing mechanism is less than satisfactory because indane, which has just as many benzylic hydrogens as tetralin, is relatively ineffective as a donor.¹⁸ Hydrogen transfer reactions in coal liquefaction have most often been depicted by stepwise mechanisms in which hydrogen is transferred sequentially, one atom at a time.

Virk and his associates^{18,19} hypothesized that the overall interaction between the coal substrate and hydrogen donor involves a sequence of concerted, pericyclic steps. In delineating a coal liquefaction mechanism, they distinguished three basic steps, namely rearrangements, hydrogen-transfer, and fragmentation. Some typical reactions appropriate for each step are indicated below using Woodward-Hoffman terminology²⁰ :

Rearrangements: sigmatropic shifts, electrocyclic reactions

Hydrogen-transfer: group-transfers

Fragmentation: group-transfers, retro-ene, cyclo-reversions

An example is the postulated pathway for thermal decomposition of 1,2-diphenylethane, shown below.¹⁹ If this mechanism is of consequence, the formation of the rearranged intermediate by a sigmatropic shift must take place at a reasonable rate. However, detailed thermochemical and kinetic analyses²¹ show that the rate of decomposition of 1,2-diphenylethane by the proposed mechanism is predicted to be roughly 18 orders of magnitude slower than the observed rate.

The reduction of aromatic compounds by hydroaromatic hydrogen donors has been proposed to take place by concerted pathways. According to the symmetry rules, the concerted transfer between certain partners is thermally allowed through transition states readily reached by suprafacial-suprafacial approach of the reactants. In other cases,

3,3' Sigmatropic Shift

Hydrogen Group Transfer

Retro-ene Fragmentation

the suprafacial-suprafacial approach leads to a transition state that is disallowed for thermal concerted transfer of hydrogen. Bass and Virk²² tested the proposition by using the pairs anthracene and 1,4-dihydronaphthalene; phenanthrene and 1,2-dihydronaphthalene (both allowed in the suprafacial approach); anthracene and 1,2-dihydronaphthalene; and phenanthrene and 1,4-dihydronaphthalene (both forbidden in the suprafacial approach). The rate constants for all pairs are found to be higher for the cases allowed in the suprafacial approach than those forbidden. King and Stock²³ have studied the hydrogen transfer reactions of 1,2- and 1,4-dihydronaphthalene, and found out that these donors are thermally unstable. The relative magnitudes for reduction by the 1,2- and 1,4-isomers were found to be contrary to prediction based on orbital symmetry rules, but in accord with expectation based on the thermochemistry of the donors. From a very thorough study of the disproportionation of 1,2-dihydronaphthalene at 300°C, Heesing and Muellers²⁴ concluded that, in the disproportionation reaction, hydrogen was transferred neither in a pairwise nor a stereospecific manner.

Although some evidence for the possible intervention of concerted reactions has been found at higher temperatures, the postulated pericyclic pathways for the model reactions investigated under liquefaction conditions thus far do not seem to bear up under the weight of experimental evidence. This does not mean that they cannot play a role in coal liquefaction or other hydrogen transfer processes, but only that the means to reveal their possible consequences have not yet been devised.

Bimolecular Step: Radical Hydrogen Transfer

In contrast to the traditional bond-scission/radical-capping liquefaction mechanism, McMillen et.al²⁵ report results that suggest the opposite. They propose that coal liquefaction is a result of hydrogen-exchange reactions, and, furthermore, a substantial portion of these transfers do not involve free hydrogen atoms. They have reported^{26,27} that a significant portion of the molecular weight decrease that occurs during donor-solvent coal liquefaction results from a bimolecular transfer of hydrogen from cyclohexadienyl-type radicals to the ipso positions of linkages to aromatic systems in coal structures, resulting in cleavage:

The results in reaction above could also be achieved by H-atom elimination, followed by addition of free H-atoms to the substrate. However, in model compound studies under conditions typical of coal liquefaction the bulk of H-transfer does not occur via "free" hydrogen atoms; instead, it is effected by cyclohexadienyl radicals in a single bimolecular step, radical hydrogen transfer (RHT)^{26,27}.

McMillen et. al²⁷ suggested the direct transfer of hydrogen atom from solvent derived radicals to substituted positions in aromatic rings as preliminary steps in depolymerization of coal structures. At 400 °C, the ipso-substituted cyclohexadienyl

radicals resulting from such H-transfer are well known to rapidly eliminate the substituent:

Five possible non-ionic mechanisms for hydrogen transfer leading to scission of strong carbon-carbon bonds in coal structure proposed are the following²⁷:

Concerted H₂-transfer

Reverse radical-disproportionation (RRD)

H-atom elimination-addition

3-step hydrogen transfer Radical hydrogen-transfer (RHT)

Of the various hydrogen transfer possibilities considered, only RHT was consistent with the evidence presented by them. They concluded that hydrogen transfer from benzocyclohexadienyl radicals in the phenanthrene and anthracene systems takes place primarily by a single bimolecular step that bypasses the production of free hydrogen atoms. Billmers et.al^{28,29} report evidence for an RHT process in a related anthracene system. Choi and Stock³⁰ also proposed a bimolecular H-transfer from a radical to a heteroatom π -system.

One of the problems with the traditional mechanism of coal liquefaction is the lack of correlation between a solvent's liquefaction effectiveness and its ability to

scavenge radicals. For example, 9,10-dihydroanthracene, which is the most effective radical scavenger among the commonly tested hydroaromatic model solvents¹⁷, is not a similarly effective solvent for coal liquefaction³¹. This is illustrated in Figure 32, in which coal conversion effectiveness is plotted against relative rates of scavenging of benzyl radical. Although 9,10-dihydroanthracene scavenges benzyl radicals about ten times more rapidly than 9,10-dihydrophenanthrene, the former is slightly less effective in coal conversion than latter.

In contrast, with the conventional thermolysis/radical-capping mechanism, a coal liquefaction mechanism incorporating RHT is capable of accomodating the fact that 9,10-dihydroanthracene is actually of similar effectiveness to 9,10-dihydrophenanthrene or 4,5-dihdropyrene, and that anthracene is much less effective than pyrene or phenanthrene. The RHT mechanism for coal liquefaction in hydroaromatic solvents is shown in the reactions below.

Initiation/termination

Propagation

Propagation net reaction

The net result of this chain sequence suggests that the stability of the intermediate radical $\text{ArH}\cdot$ largely cancels out. The principal noncancelling factors that promote the net reaction are decreasing stability of ArH_2 and increasing stability of Ar . McMillen et.al²⁵ derived an expression for the estimated relative cleavage rate (k_{clv}) of a given substrate in a series of ArH_2 solvents by the steady-state analysis. The derivation gives

$$k_{\text{clv}} \propto \exp\left\{\left[\frac{1}{n}\Delta H_f^\circ(\text{ArH}_n-\text{Ar}) + a\Delta H_f^\circ(\text{Ar}-\text{ArH}\cdot)\right]/RT\right\}$$

where $n=2$ or 4 for dihydro- or tetrahydroaromatics, respectively. The relative values of estimated k_{clv} for some commonly used solvents are compared with the relative extents of coal conversion. They do not exactly match with each other, but they are far closer than the relative rates measured for radical scavenging.

It would not be right to suggest that spontaneous C–C or C–O bond scission (thermolysis) is unimportant in liquefaction. The very class of bond scission reactions discussed above cannot take place without prior radical formation. The prior bond scission must either be thermolysis or reverse radical disproportionation. Therefore, either reverse radical disproportionation or the spontaneous scission of existing weak links in

the coal structure can induce the scission of other linkages too strong to undergo thermolysis. The bond cleavage resulting from hydrogen transfer by RHT is a major contributor to the liquefaction process in the more effective solvent system.

Conclusion

The mechanisms of hydrogen transfer from donor solvents to various coal structures remain largely unspecified although many researchers have investigated. Much discussion of donor solvent coal liquefaction is based on the conventional principal mechanism that involves thermal scission of covalent bonds, followed by capping the free radicals by hydrogen atom abstraction from the donor solvent. This has continued although a number of researchers have pointed out alternative possibilities. Those are radical chain processes (usually involving β -scission of the chain carriers), hydrogen atom and radical addition-elimination processes, hydride transfer, and concerted H_2 -transfer processes. Recently, the importance of direct transfer of hydrogen atom from solvent derived radicals to substituted positions in aromatic rings as preliminary steps in depolymerization of coal structures has been emphasized. Therefore, one cannot ignore one mechanism over the other. Under the circumstances, all possibilities have to be considered.

References

1. Whitehurst, D.D., Mitchell, T.O., Farcasiu, M. Coal Liquefaction, Academic Press, New York, (1980).
2. Bockrath, B.C. in Coal Science, vol.2, pp.65-124, (1982).
3. Curran, G.P., Struck, R.T. and Gorin, E., *Ind.Eng.Chem.Process Dev.Div.*, 6, 166, (1967).
4. Obara, T., Yokono, T. and Sanada, Y. *Fuel* 62, 813, (1983).
5. Gorin, E. in Elliott, M.A.(ed.): Chemistry of Coal Utilization, 2nd suppl.vol., J. Wiley & Sons, New York, pp.1845-1918, (1981).
6. Neavel, R.C., *Fuel* 55, 237, (1976).
7. Neavel, R.C., *Philos. Trans. R. Soc. London, Ser.A.*, 300, 141, (1981).
8. Burgess, C.E., M.S. Thesis, The Pennsylvania State University, (1991).
9. Kubo, J., *Fuel Proc. Tech.*, 27, 263, (1991).
10. Kubo, J., *Fuel Proc. Tech.*, 28, 19, (1991).
11. Song, C., Lai, W-C., and Shobert, H.H., paper submitted in 204th ACS National Meeting, Washington, D.C., Aug.23-28, (1992).

12. Coleman, M.M., Selvaraj, L., Sobkowiak, M., and Yoon, E., *Energy & Fuels* (1992) in press.
13. Petrakis, L. and Grandy, D.W., *Fuel* , 60 , 1017, (1981).
14. Sprecher, R.F. and Retcofsky, H.L., *Fuel* , 62 , 473, (1983).
15. Stock, L.M. in Schlosberg, R.H., Chemistry of Coal Conversion, Plenum Press, New York, 253, (1985).
16. Poutsma, M.L., *Energy & Fuels* , 4(2) ,113, (1990).
17. Bockrath, B., Bittner, E., McGrew, J., *J. Am. Chem. Soc.*, 106 , 135, (1984).
18. Virk, P.S., Bass, D.H., Eppig, C.P., Ekpenyong, D.J. *Am. Chem. Soc. Div. Fuel Chem. Prepr.* 24(2) 144, (1979).
19. Virk, P.S., *Fuel* 58, 149, (1979).
20. Woodward, R.B., Hoffmann, R. The Conservation of Orbital Symmetry, Verlag Chemie GmbH, Weinheim, (1970).
21. Stein, S.E. *Fuel*, 59, 900, (1980)
22. Bass, D.H. and Virk, P.S. *Am. Chem. Soc. Div. Fuel Chem. Prepr.* 25(1), 17, (1980).
23. King, H.H. and Stock, L.M., *Fuel* 60, 748, (1981).
24. Heesing, A., and Muellers, W., *Chem. Ber.*, 113, 9, (1980).
25. McMillen, D.F., Malhotra, R., Hum, G.P., and Chang, S-J, *Energy & Fuels* 1 193, (1987).
26. McMillen, D.F., Chang, S-J, Nigenda, S.E., Malhotra, R., *American Chemical Society, Division of Fuel Chemistry, Preprints:* 30(4) 414, (1985).
27. McMillen, D.F., Malhotra, R., Chang, S-J, Nigenda, S.E., Ogier, W.C., Fleming, R.H., *Fuel* 66 ,1611, (1987).
28. Billmers, R.L., Griffith, L.L., Stein, S.E., *American Chemical Society Division of Fuel Chemistry, Preprints:* 30(4) ,283, (1985).
29. Billmers, R.L., Griffith, L.L., Stein, S.E., *J. Phys. Chem.* 90, 517,(1986).
30. Choi, C-Y and Stock, L.M., *J. Org. Chem.* 40, 2871, (1984).
31. Curtis, C.W., Guin, J.A., Kwon, K.C., *Fuel* 63 ,1404, (1984).

Task 5. Exploratory Studies on the Direct Conversion of Coal to High Quality Jet Fuels.

1. Production of Jet Fuels from Coal (Contributed by Caroline Burgess)

Introduction

Cycloalkanes (cyclohexanes and decalins) are components of jet fuel that possess a high thermal stability [1]. Using coal as the parent material to produce these compounds is desirable because coals contain aromatic and hydroaromatic that in principle could be hydrogenated to cycloalkanes. Coals are diverse in composition, so it is necessary to characterize candidate feedstock coals to determine the best (in the sense of having high populations of small aromatic units that could be converted to the desired cycloalkanes) ones to produce jet fuels. It is then necessary to compare the products from liquefaction the optimum reaction conditions and the best catalyst to use for the production of high quantities of thermally stable jet fuel.

Experimental

The work to date is with two coals; the coals are DECS-6 (Blind Canyon) and DECS-12 (Pittsburgh #8). Analyses of these coals are shown in Table 7. The coals were reacted at two different reaction conditions for baseline experiments. The reactions were carried out in microautoclave reactors and heated in fluidized sandbaths as described in previous reports [1]. The experimental conditions were 360 °C for 1 h and 425 °C for 1 h. For each reaction, the reactor contained 10g of dried coal and 10g of pyrene and was pressurized to 1000 psi H₂ (cold). The products were removed from the reactor with dichloromethane (DCM) and Soxhlet extracted until the solvent was colorless (24-36 h), then extracted with tetrahydrofuran (THF) until the solvent was colorless. The residue was rinsed with acetone and then pentane and dried at 100 °C for 12 h to remove remnants of solvents and water. The DCM solubles were then distilled to between 85-125 °C at a vacuum pressure of 140 mm Hg (equivalent to a ≈180-200 °C atmospheric distillation fraction), but there were such small quantities of liquid obtained that a new distillation apparatus would be set up to increase the vacuum in order to obtain a more realistic jet fuel fraction cut. For the reactions at 360 °C, no distillation was done and the hexane solubles were collected for analysis. For the reactions at 425 °C, the distillate was collected for analysis and the remaining undistilled sample was extracted with hexane. The conversion was calculated and the preasphaltene (THF soluble-DCM insoluble) and asphaltene + oil + gas yields were determined.

Table 7: Elemental analysis, maceral composition, and NMR data for DECS-6 and -12.

Name	Blind Canyon DECS-6	Pittsburgh 8 DECS-12
Rank	hvA Bituminous	hvA Bituminous
Elemental Composition		
%C	81.72	84.72
%O	10.10	7.37
%H	6.22	5.66
%S	0.40	0.83
%Mineral Matter	6.67	11.88
Maceral Composition		
%Vitrinite	69.1	83.0
%Liptinite (Resinite)	17.0 (5.0)	8.1 (2.6)
%Inertinite	13.6	8.9
f_a (aromaticity)	0.697	0.690
f_a^h (protonated carbon)	0.412	0.290

The coals and residues were analyzed by flash pyrolysis GC/MS and ^{13}C -NMR (CPMAS and dipolar dephasing experiments) as described in previous reports [1]. The ^{13}C -NMR spectra are shown in Figures 33 and 34, and the flash pyrolysis GC/MS chromatograms are Figures 35-39. The hexane soluble samples and distillates were analyzed by GC and GC/MS as described in previous reports [1]. The GC/MS chromatograms of the hexane soluble fractions are Figures 40-42. Because of the use of pyrene as the coal liquefaction solvent, analysis of products was not as straightforward. The flash pyrolysis of the residues clearly indicated that not all the pyrene was completely extracted. Because of the high proportion of pyrene in the hexane solubles, the hexane solubles were only analyzed up to the elution time of pyrene to prevent damage to the mass spectrometer.

Results and Discussion

The ^{13}C -NMR of the coals indicates that Pittsburgh #8 (DECS-12) is more aromatic than Blind Canyon (DECS-6). Both coals contain phenol and ether functional groups, while DECS-6 also contains carbonyl and carboxyl functional groups. While the ^{13}C -NMR data is good for determining general information on functional groups, the flash pyrolysis GC/MS is useful for detecting the presence of certain types of compounds as the sample pyrolyzes, hence, providing more specific information. The main difference between the two coals, as observed by NMR data, is that DECS-6 is relatively more alkane-like than DECS-12.

The conversion results are shown in Table 8 and Figure 43. The bar graph in Figure 40 emphasizes the increase in conversion when the reaction was done at 425 °C compared to 360 °C. It also shows that the increase in conversion is actually accompanied by a decrease in the yield of THF soluble-DCM insolubles and an increase in the DCM solubles + gas for the reaction at 425 °C relative to the reaction at 360 °C. The analysis of the residues, the hexane-soluble fraction and distillate reflect the changes that occur from raw coal to the reaction at 360 °C to the reaction at 425 °C. For DECS-6, the NMR data and the flash pyrolysis data of the raw coal indicate a high percentage of alkanes, with some occurrence of phenol, alkyl phenols, alkyl benzenes, and alkyl naphthalenes. For the residue produced from the 360 °C reaction, some of these components (i.e. phenols, alkyl naphthalenes, alkyl benzenes, and alkanes/alkenes) are no longer observed in the residue flash pyrolysis and NMR, but there is an increase in some of these same compounds in the hexane-soluble fraction (i.e. phenols, alkyl benzenes, and alkyl naphthalenes) as shown in the GC/MS. For the residue produced from the 425 °C reaction, there are even fewer products of pyrolysis (i.e. alkanes/alkenes), while the hexane-soluble fraction has definite increase in alkanes, alkyl naphthalenes, and prist-1-ene. A similar comparison can be done for DECS-12, but the products that dominate the flash pyrolysis products for the raw coal are phenols, alkyl naphthalenes, and alkyl benzenes and not the alkanes. The loss of these compounds is reflected in the flash pyrolysis of the residues at 425 °C, and the corresponding increase is noted in the GC/MS of the distillate and hexane-soluble fraction at 425 °C. One question to be answered is whether the liquefaction products come entirely from the "mobile phase" of the coal, or whether some of the products come from the cracking of the heavier THF soluble/DCM insoluble fraction or from the coal itself.

Table 8 Conversion data for thermal reactions of DECS-6 and -12.

Experiment #	Coal	Reaction Cond	Conversion	THF Sol/DCM Insol	DCM Sol + Gas
TB12-1A	Pittsburgh #8	360°C, 1h, pyrene	42.1	20.0	22.1
TB12-2		425°C, 1h, pyrene	60.0	11.7	48.4
TB6-1	Blind Canyon	360°C, 1h, pyrene	43.1	21.7	21.4
TB6-2		425°C, 1h, pyrene	66.9	11.3	55.6

Future Work

More work will be done with three additional coals, as well as some experiments to determine the mechanism of the thermal reaction. Analysis of the heavy products (THF soluble/DCM insoluble) will be possible with new equipment being obtained (high pressure liquid chromatography and supercritical fluid chromatography). The next phase of the project is to test catalyst and reaction conditions to produce high yields of liquids boiling in the jet range. As noted in the previous section, such high yields cannot be made under entirely thermal reaction conditions.

References

1. Song, C., Eser, S., Schobert, H.H., Hatcher, P.G., Coleman, M.M., and Walsh, P.M. Advanced Thermally Stable Coal-Derived Jet Fuels, Quarterly and Annual Reports, July 1989-November 1992.

2. Hydrogenation/dehydrogenation Reactions of Rosin (contributed by Richard Dutta)

Introduction

Cycloalkanes are desirable components of advanced jet fuels because of their high thermal stability. If cycloalkanes can be produced in high yield by direct liquefaction, downstream processing of the product would be reduced. Resinite is known to be made up of predominantly aliphatic and hydroaromatic structures. It can be characterized and classified depending on its structure and origin. One major class of resinite is diterpenoid in nature. If the behavior of diterpenoids under liquefaction conditions can be determined and understood, a highly efficient liquefaction system can be developed. Coals with a high resinite concentration can be liquefied, and the cycloparaffinic products from resinite can be extracted into the oil fraction and into the jet fuel boiling range. The liquid produced should be thermally stable and could be a high quality jet fuel.

However, because resinite is a very complex mixture of polymerized diterpenoids, it is advisable to study model compounds. This makes analysis of products easier and evaluation of reaction pathways less complicated. Rosin is commercially available and contains 90% diterpenoids (isomeric with abietic acid). In a sense, rosin is a simplified resin and its hydrogenation/dehydrogenation behavior should give an insight into resinite liquefaction.

Experimental

Rosin gum was used as reactant in all the reactions. All reactions were carried out in standard microautoclave reactors under 1000 psi hydrogen pressure. Reactions were carried out at varying temperatures and times of reaction. The products were dissolved in acetone and analysed by GC/MS. Quantitation of the concentration of the products was done using the internal standard method.

Results and Discussion

Figures 44-47 show the major compounds in the reaction products of rosin hydrogenation at various temperatures. Figure 48 shows the concentration of reaction products and how they vary with temperature. The chromatograms can be split into three major sections:

- 1) 0-20 minutes - Benzenes.
- 2) 20-40 minutes - Naphthalenes.
- 3) 40-60 minutes - 3-ring compounds.

At 350° C the major products of reaction are 3-ring compounds.e.g. norabietatriene. This compound is formed by dehydrogenation of abietic acid (a major component of rosin). Norabietatriene is further dehydrogenated to tetrahydroretene and retene. At this low temperature, only a small amount of retene is formed. Cracking of the 3-ring compounds is minimal, with only C₄-benzene and isopropyltetralin being formed in large concentration.

At 400°C the concentration of norabietriene increases with increasing dehydrogenation of abietic acid. This also yields an increase in tetrahydroretene and retene in the reaction products. Although difficult to see from Figure 45, the concentration of benzenes triples in the products. This can be accounted for by the cracking of the saturated ring of isopropyltetralin produced at 350°C. The concentration of naphthalenes has not increased. This is because the temperature is not yet high enough for major cracking of the 3-ring compounds. In theory, cracking of norabietatriene will occur at the saturated terminal ring, giving naphthalenes. This does not occur at 400°C.

At 450°C it can be seen that compounds that appear in region 2 of the chromatograph are now being formed. These naphthalenes are cracking products of norabietatriene, tetrahydrotetene, and other 3-ring compounds. It is unlikely that the fully aromatic retene has cracked. It is widely held that all hydrocracking reactions go in two stages: first, hydrogenation of the terminal ring, and then cracking of the saturated ring. Certain catalysts promote cracking at the central ring to form biphenyl but under the present conditions this is not observed. Figure 48 shows the concentration of norabietettriene and tetrahydrotetene decreasing after 400°C. This is in line with the thoughts that it is these compounds that are cracking to benzenes and naphthalenes and not retene which continues to increase.

If we interpret the chromatograms purely from the point of view wanting to produce a good quality jet fuel, it appears that hydrocracking of the 3-ring compounds is the route to take. Naphthalenes and benzenes are produced from 3-ring compounds. These compounds can form the backbone of something to work with (i.e., material susceptible to hydrogenation) to produce desirable cycloalkanes and tetralins. Unfortunately these cracking reactions occur at high temperatures, which is accompanied by increasing dehydrogenation of the cycloparaffinic diterpenoids. In a sense we are destroying the major property of these compounds that they were selected for—their cycloparaffinic nature. The fully aromatic retene and phenanthrene seen in large concentration at 450 and 500°C are likely precursors to solid deposits in thermally stressed jet fuel.

The reaction at 500°C has almost totally cracked the 3-ring compounds in rosin to naphthalenes and benzenes. Cleavage of side chains has also occurred. This may seem a good reaction if jet fuel is to be produced, but the amount of dehydrogenation makes the feasibility of this reaction being of any use, small. Continuing work may prove otherwise. For example, is it possible to re-hydrogenate the aromatic compounds to compounds that are desirable and can be hydrocracked? It is likely that in going to such a high temperature, we are simply "going backwards to go forward".

The results of the reactions of rosin at 450°C and for times up to 60 minutes can be seen in Figures 49-52. Figure 53 shows how the concentrations of the products vary with time of reaction. It can be seen that cracking does not occur to a great extent until after 30 minutes. This is simultaneous with the disappearance of norabietettriene and tetrahydrotetene. The concentration of retene continues to increase even as the concentration of naphthalenes increases from 0.2–1.8 mg/ml. This is further evidence that retene does not crack, although its concentration may be kept down due the fact that tetrahydrotetene is being hydrocracked. The reason for investigating the way rosin

behaves under differing times of reaction comes from ideas promoted from the temperature variation of reactions. To produce compounds that make good jet fuel from diterpenoid structures, it is necessary to hydrocrack the 3-ring compounds to naphthalenes and benzenes. This needs a high temperature, which also promotes dehydrogenation of cycloparaffinic compounds to unwanted fully aromatic compounds. Therefore, a two stage reaction is envisaged:

- 1) A high temperature cracking reaction to yield a "backbone" of naphthalenes and benzenes. This means a reaction temperature of at least 450°C (and maybe as high as 500°C) and a reaction time of at least 45 minutes.
- 2) A low temperature hydrogenation stage. The naphthalenes and benzenes from stage 1 would be catalytically hydrogenated to cycloalkanes and tetralins. The final products should fall into the jet fuel boiling range yielding a highly thermally stable fuel.

From the above results, reaction pathways have been proposed (Figures 54,55). Figure 54 deals with the dehydrogenation pathway of abietic acid. One aspect of the reaction, the decarboxylation of abietic acid, has not been dealt with in this discussion. It is hoped that future work will clarify the exact nature of this and how it affects the hydrocracking reaction. In future work, liquid NMR of products will be used in conjunction with GC/MS to give an idea of what is happening to the acid functionality. Figure 55 deals with the possible route of cracking of the 3-ring compounds.

Ongoing and future work will deal with catalytic hydrocracking of rosin. NiMo/Al₂O₃, a Ni-zeolite catalyst and a dispersed catalyst (ammonium tetrathiomolybdate) will be tested.

3. Temperature-programmed Liquefaction of Coals Using Bimetallic Dispersed Catalysts from Organometallic Complexes (Contributed by Chunshan Song and Derrick Parfitt).

Introduction

It has been recognized recently that dispersed catalysts are superior to supported catalysts for primary coal liquefaction. Most previous work involved dispersed molybdenum sulfide from a water-soluble salt [Derbyshire, 1988]. Some organometallic compounds including metal carbonyls and naphthenates have also been tested as catalyst precursors [Suzuki et al., 1987; Herrick et al., 1990; Swanson, 1992], which often requires the addition of sulfur compounds [Yamada et al., 1985]. There are some unique advantages of organometallic compounds as catalyst precursors. First, most organometallic compounds are soluble in hydrocarbon solvents and may be used as oil-soluble precursors. Second, as has been demonstrated by Hirschon and Wilson [1991,

1992], some organometallic compounds can be easily decomposed to metal sulfides at low temperatures. The present work is concerned with organometallic precursors which can directly produce metal sulfides upon thermal decomposition.

Little work on bimetallic dispersed catalysts for coal liquefaction has appeared, although previous work on multicomponent catalysts has involved the mixture of two or more inorganic salts [Garg and Givens, 1984; Song et al., 1986, 1991; Sommerfeld et al., 1992]. Related to this work is a general observation from previous investigations that there could be synergistic effects between different metals, and an organometallic precursor may be better than an inorganic one. Our interest in the heteronuclear organometallic compounds was stimulated by the recent book on metal clusters published by Mingos and Wales [1990]. It seemed to us that highly active catalysts might be prepared from some clusters containing metal-metal bonds, especially the "thiocubane" clusters containing two metals such as Fe or Co and Mo in a single molecule.

Two different metals bound together in a single compound should have a more systematic spatial arrangement in the resulting catalytic phase upon thermal decomposition than if two separate compounds were used to introduce the two different metals to a catalytic system. The present work is an exploratory study of bimetallic dispersed metal sulfide catalysts for coal liquefaction, involving the synthesis of the organometallic thiocubane clusters that contain Mo and Co as well as sulfur in a single molecule, and liquefaction of coal impregnated with the precursors under non-programmed and temperature-programmed (TPL) conditions, where the programmed heat-up serves as a step for both catalyst activation and coal pretreatment or preconversion. The advantages of temperature-programmed conditions have been demonstrated in our recent work [Song et al., 1992; Song and Schobert, 1992; Huang et al., 1992].

Experimental

1. Catalyst precursors and coal samples. Three bimetallic thiocubanes were used as catalytic precursors: $\text{Mo}_2\text{Co}_2\text{S}_4(\text{S}_2\text{CNEt}_2)_2(\text{CH}_3\text{CN})_2(\text{CO})_2$ [MoCo-TC1], $\text{Mo}_2\text{Co}_2\text{S}_4\text{Cp}_2(\text{CO})_2$ [MoCo-TC2], and $\text{Mo}_2\text{Co}_2\text{S}_4(\text{Cp}^*)_2(\text{CO})_2$ [MoCo-TC3], in which Et, Cp and Cp^{*} represent ethyl group, cyclopentadiene, and pentamethylcyclopentadiene, respectively. These thiocubanes were synthesized in our laboratory based on the procedures of Brunner and Watcher [1982] and Halbert et al. [1985]. For comparative examination, bimetallic metal sulfide complex, cobalt bis-tetrathiomolybdate trianion was also synthesized based on the procedure of Pan et al. [1985]. The trianionic compound, $(\text{PPh}_4)_3\text{Co}(\text{MoS}_4)_2$, is designated as MoCo-S.

The U.S. Department of Energy Coal Samples (DECS, #9 and #12) were obtained from the Penn State/DOE Coal Sample Bank. The Montana subbituminous coal (DECS-9, PSOC-1546, < 60 mesh) has the following composition: 24.7% moisture, 4.8% ash, 33.5% volatile matter, and 37.1% fixed carbon on an as-received basis; 76.1% carbon, 5.1% hydrogen, 0.9% nitrogen, 0.3% organic sulfur, and 17.5% oxygen on a dmmf basis. The Pittsburgh #8 bituminous coal (DECS-12, PSOC-1549, < 60 mesh) has the following composition: 2.4% moisture, 10.0% ash, 35.2% volatile matter, and 52.4% fixed carbon on an as-received basis; 84.8% carbon, 5.7% hydrogen, 1.4% nitrogen, 0.7% organic sulfur, and 6.5% oxygen on a dmmf basis. The coals were dried for two hours at 100°C in a vacuum oven before use.

2. Incipient wetness impregnation of catalyst precursors. The catalytic precursors were dispersed on to the coal by the incipient wetness impregnation (IWI) method using organic solvents. IWI method was applied to coal in a previous work [Huang et al., 1992]. Because of the difference in the solubility of the organometallic precursors, several solvents including toluene, THF, CHCl_3 and acetonitrile were used for dissolving them. The organic solution of a precursor was intermittently added dropwise to the dried coal in a 100 mL beaker, in a fashion that the wet spots over the coal particles do not touch each other, followed by manual stirring with a glass rod until all signs of wetness disappeared. In order to keep the metal loading from different precursors at a constant level, we first estimated the incipient wetness volume prior to the catalyst impregnation with a given solvent, which means the total volume of the solvent needed to reach the point of incipient wetness: the point when the solution drops begin to remain on the external surface of the coal. The loading for the bimetallic thiocubanes was 0.5-0.6 wt% of molybdenum on the basis of dmmf coal. The impregnated coal sample was dried at 100°C for 2 h in a vacuum oven. IWI method is often used for loading inorganic salts from their aqueous solution on to a catalyst support without [Solar et al., 1991]. It should be noted that the IWI method used in our work is different from conventional one in that we only use certain amount of solution defined by the estimated incipient wetness volume to achieve a constant metal loading.

3. Liquefaction under SSL and TPL conditions. All reactions were carried out in 25 mL tubing bomb microautoclaves in a temperature-controlled fluidized sandbath. Each reaction used approximately 3 g dried coal. 1-Methylnaphthalene was used as the reaction solvent (3 g) unless otherwise mentioned. In several experiments tetralin was also used as a hydrogen-donor solvent (3 g) for comparison. The initial H_2 pressure was 7 MPa at room temperature for all the runs. For catalyst screening, single-stage liquefaction (SSL) was performed, where the tubing bomb was rapidly heated to the

prescribed temperatures (400-425 °C) for 30 minutes (plus a three minute heat-up period) followed by a rapid quench in cold water bath. Temperature-programmed liquefaction (TPL) had the tubing bomb rapidly heated up to a low temperature (275°C in all the catalytic runs, 200°C in the thermal runs) and soaked at that temperature for 30 minutes before the temperature was gradually increased (5-7°C/min) to a higher temperature (400°C-425°C) and held there for 30 minutes before rapid quenching with cold water bath. These procedures were established in our recent work [Song and Schobert, 1992; Huang et al., 1992].

The gaseous product was vented after the reaction was complete and the liquid and solid products were washed into a tared ceramic thimble with hexane. The products were separated under a N₂ atmosphere by Soxhlet-extraction using hexane, toluene, and THF in succession. Solvents were removed by rotary evaporation, and the products were dried in vacuum at 100°C for 6 h except for the hexane-solubles. The asphaltene (toluene soluble, but hexane insoluble), preasphaltene (THF soluble, but toluene insoluble), and residue were weighed and the conversion and product distribution were calculated based on dmmf coal. All the runs were repeated at least once or twice to confirm the reproducibility. In most cases, the experimental errors were within ± 2 wt% for conversion, and the average data are reported here.

Results and Discussion

1. Effects of precursor type and solvents for impregnation. Table 9 shows the results of liquefaction of the Montana subbituminous coal at 400°C for 30 min. We first prepared and tested Mo₂Co₂S₄(S₂CNEt₂)₂(CH₃CN)₂(CO)₂ [MoCo-TC1], which was first synthesized and used recently by Halbert et al. [1991] in preparing MoCo hydrotreating catalyst. Using MoCo-TC1 impregnated on to DECS-9 coal from acetonitrile, however, showed little catalytic effect for increasing conversion. Replacing CH₃CN with THF for impregnating MoCo-TC1 increased coal conversion relative to the thermal run by 14 wt%, but did not improve oil formation to any significant extent. It seems that the acetonitrile solution and the dithiocarbamate and acetonitrile ligands in MoCo-TC1 can poison the resulting catalyst under the conditions employed. This observation prompted us to prepare the thiocubane which contains no nitrogen in the ligands, leading to the synthesis of Mo₂Co₂S₄Cp₂(CO)₂ [MoCo-TC2], and Mo₂Co₂S₄(Cp'')₂(CO)₂ [MoCo-TC3]. The basic difference between these three thiocubanes is the type of ligands to the Mo [Cp = C₅H₅, Cp'' = C₅Me₅; all the five (ring) carbon atoms are equidistant from the metal atom].

Table 9. Liquefaction of DECS-9 Montana Subbituminous Coal at 400°C for 30 min

Catalyst precursor	Solvent for catalyst impregn ^a	Reaction solvent ^b	Reaction condition	Oil + Gas dmmf wt%	Asphalt. dmmf wt%	Preasph. dmmf wt%	Tot Conv dmmf wt%
None	None	1-MN	SSL	16.0	9.4	6.8	32.2
MoCo-TC1	CH ₃ CN	1-MN	SSL	22.8	4.8	5.2	32.8
MoCo-TC1	THF	1-MN	SSL	18.7	12.8	14.8	46.3
MoCo-TC2	Toluene	1-MN	SSL	32.4	18.0	24.2	74.6
MoCo-TC2	THF	1-MN	SSL	25.8	17.9	23.7	67.4
MoCo-TC3	Toluene	1-MN	TPL	33.8	17.8	19.9	71.5
MoCo-S	CHCl ₃	1-MN	SSL	21.3	12.6	16.0	49.8

a) The impregnating solvent was removed by evaporation in vacuum before reaction.

b) 1-MN was added as reaction solvent after the impregnating solvent was removed.

MoCo-TC2 impregnated from toluene afforded much higher conversion and oil yield; it appears to be much more active than MoCo-TC1. MoCo-TC3 exhibited slightly lower catalytic activity compared to MoCo-TC2. It was expected that MoCo-TC2 would afford greater conversion when THF was used as the impregnating solvent, since THF is a better swelling solvent and can penetrate the coal structure, which would improve the dispersion of the resulting Co-Mo bimetallic sulfide catalyst. Surprisingly, the catalytic liquefaction using MoCo-TC2 gave both higher oil yields and total conversion when toluene was used rather than THF. The structure and ligands of MoCo-TC3 and MoCo-TC2 are of the same nature, except that cyclopentadiene in MoCo-TC2 is substituted by pentamethylcyclopentadiene in MoCo-TC3. There was a small increase in the oil yield coupled with a decrease in preasphaltene yield when MoCo-TC3 was used in temperature-programmed liquefaction. Table 10 presents the results of catalytic runs of DECS-9 coal at 425°C. The order of catalytic activity at 425°C is the same as that observed from runs at 400°C: MoCo-TC2 > MoCo-TC3 > MoCo-TC1.

In an attempt to examine the role of bonding between Co and Mo, we further prepared and tested heterometallic cluster of the form $\text{Co}(\text{MoS}_4)_2^{3-}$ which has distinctly different structure than the above-mentioned thiocubanes. Comparing results in Table 9 and Table 10 reveals that MoCo-S is more active than MoCo-TC1 at both 400 and 425°C but is much less active compared to MoCo-TC2, regardless of the impregnating solvent.

Table 10. Liquefaction of DECS-9 Montana Subbituminous Coal at 425°C for 30 min

Catalyst precursor	Solvent for catalyst impregn	Reaction solvent	Reaction condition	Oil + Gas dmmf wt%	Asphalt. dmmf wt%	Preasph. dmmf wt%	Tot Conv dmmf wt%
None	None	1-MN	SSL	16.7	16.4	13.8	46.9
MoCo-TC1	THF	1-MN	SSL	20.3	9.9	5.7	35.9
MoCo-TC2	Toluene	1-MN	SSL	42.3	14.9	14.8	72.0
MoCo-TC2	THF	1-MN	SSL	36.5	15.5	18.0	70.0
MoCo-TC3	Toluene	1-MN	SSL	36.7	11.9	13.2	61.4
MoCo-S	CHCl ₃	1-MN	SSL	34.9	11.1	13.2	59.2

Table 11 shows the effect of using the catalytic precursors on liquefaction of DECS-12 Pittsburgh #8 bituminous coal. At 400°C, the catalytic effects appear to be enhanced conversion to preasphaltene and asphaltene, with little increase in oil production relative to the thermal run. At 425°C, using MoCo-TC2 increased conversion significantly compared to the thermal run; it also promoted oil production moderately. However, increasing temperature from 400°C to 425°C caused a decrease in conversion both in thermal and catalytic runs. In both cases, MoCo-TC2 was much more active than MoCo-TC1, although the latter was used under better conditions (TPL) than the former (SSL), as we further describe below. This again points to the negative impact of the CH₃CN and S₂CNEt₂ ligands in MoCo-TC1 upon the resulting catalyst in coal liquefaction. Therefore, it appears that an active MoCo bimetallic sulfide catalyst is generated in situ from MoCo-TC2 during liquefaction. Under comparable conditions the catalyst from MoCo-TC1 is much less active, although an active catalyst could be generated also from this precursor if first decomposed at low temperature followed by venting and purging to remove poisonous compounds and followed by re-charging H₂ gas and heat-up.

By combining Tables 9, 10 and 11, it becomes very clear that MoCo-TC2 is the best precursor and MoCo-TC1 is the worst precursor among the three thiocubanes, which differ from each other only in the type of ligands to Mo. Bimetallic sulfide complex MoCo-S also produces a catalyst whose activity is lower than that from MoCo-TC3 at 400°C and close to MoCo-TC3 at 425°C. In MoCo-S, the Co and Mo are bound through sulfur-bridge bonding, but in MoCo-TC2 or TC3, there are direct metal-metal bonds between Co-Mo, Co-Co, and Mo-Mo in addition to the sulfur bridges. The superiority of

Table 11. Liquefaction of Pittsburgh #8 Bituminous Coal in 1-MN at 400-425°C

Catalyst precursor	Solvent for catalyst impregn	Reaction temp °C	Reaction condition	Oil + Gas dmmf wt%	Asphalt. dmmf wt%	Preasph. dmmf wt%	Tot Conv dmmf wt%
None	None	400	SSL	13.7	20.4	26.8	60.9
MoCo-TC1	THF	400	TPL	9.8	21.9	34.0	65.7
MoCo-TC2	Toluene	400	SSL	14.5	27.8	34.3	76.6
None	None	425	SSL	16.2	19.1	16.1	51.4
MoCo-TC1	THF	425	TPL	16.9	24.6	19.4	60.8
MoCo-TC2	Toluene	425	SSL	21.8	27.7	23.8	73.3

MoCo-TC2 over MoCo-S may suggest the importance of direct metal-metal bonding; the differences between the three thiocubanes clearly indicate the importance of ligand type. The solvents used for loading the precursors are also influential. Both toluene and THF were tested for impregnating MoCo-TC2 but the non-polar solvent seems to be better in terms of higher oil yield; the optimum solvent and method for loading catalyst are not known yet. In summary, the above results indicate that both the ligands to the metal species and the type of bonding between the two metals affect the activity of the resulting bimetallic MoCo sulfide catalyst significantly. For a given precursor, the solvent used for catalyst impregnation also affects coal conversion, although the impregnating solvent was removed before reaction.

2. Effects of temperature-programming. The second major aspect of this study is to optimize the performance of promising catalysts selected from screening tests described above. As a means to increase conversion, the liquefaction of coals impregnated with the precursors was carried out under temperature-programmed (TPL) conditions, where the programmed heat-up serves as a step for both catalyst activation (precursor decomposition to active phase) and coal pretreatment or preconversion.

Table 12 shows the effects of temperature-programming on the catalytic and thermal runs of both DECS-9 and DECS-12 coals. In the presence of either MoCo-TC2 or MoCo-TC3, TPL runs in 1-MN always give higher conversions and higher oil yields than the corresponding SSL runs. At a final reaction temperature of 425°C with 1-MN solvent, TPL runs of both DECS-9 and DECS-12 coals using MoCo-TC2 or TC3 gave 13-15 wt% higher conversions and 5-11 wt% higher oil yields than the corresponding SSL runs. Most of the trends observed from Table 4 can be rationalized based on a

general reaction model for liquefaction presented in recent papers [Song et al., 1989, 1991].

The first question that arises is why programmed heat-up is better than rapid heat-up. The superiority of TPL over SSL in catalytic runs with 1-MN solvent could be due to 1) more products from coal after longer residence time irrespective of catalyst, since a programmed heat-up is included in TPL but SSL only involves a very rapid heat-up in about three minutes followed by reaction at 400 or 425°C; 2) due to reactions including precursor decomposition and catalytic reactions during programmed heat-up. The first is not the case, as demonstrated by the fact that in the non-catalytic runs in 1-MN, using temperature programmed heat-up had essentially no impact on the liquefaction of DECS-9, neither on total conversion nor on product distribution, as can be seen from Table 4. The desirable effects of TPL, therefore, are associated with low-temperature catalytic hydrogenation reactions during programmed heat-up.

It is interesting to note from Table 12 that under TPL conditions using 1-MN solvent, increasing final temperature of all the catalytic runs from 400 to 425°C further increased coal conversions and oil yields considerably. In distinct contrast, under SSL conditions, increasing temperature of the catalytic runs (using MoCo-TC2, TC3) from 400 to 425°C caused marked decrease in the total conversions, which is a remarkable sign of significant retrogressive reactions. As pointed out by Song et al. [1989], the rate of coal thermal fragmentation is influenced by temperature and heating rate; very fast heating to high temperature would lead to extremely rapid fragmentation of coals that may exceed the capacity or rate of hydrogenation (H-donation) of the system, leading to significant retrogressive crosslinking. It is also likely that under SSL conditions (heating rates, $\geq 100^\circ\text{C}/\text{min}$) very fast radical formation occurs before transformation of MoCo-TC2 into active phase is completed, resulting in an unbalance between the rate of radical formation and the rate of radical-capping by H from catalyst surface, especially at higher temperature. In TPL runs, however, the catalyst precursor decomposes to form active bimetallic sulfide and the weak linkages are broken and stabilized during programmed heat-up, so that at the time the radical formation becomes considerable at high temperature (425°C), the catalyst is already activated and can provide dissociated hydrogen atom to cap the thermally generated radicals. These mechanistic considerations account for why using MoCo-TC2 or TC3 affords further increased conversion and oil yield under TPL conditions but gives decreased conversion under SSL conditions when the final reaction temperature is increased from 400 to 425 °C.

Table 12. Effect of Temperature Programming on Coal Liquefaction Using Bimetallic Thiocubane Precursors MoCo-TC2 and MoCo-TC3**

Catalyst precursor	Solvent for catalyst impregn	Reaction solvent	Reaction condition	Oil + Gas dmmf wt%	Asphalt dmmf wt%	Preasph. dmmf wt%	Tot Conv dmmf wt%
DECS-9 Montana Subbit Coal							
None	400	1-MN	SSL	16.0	9.4	6.8	32.2
None	400	1-MN	TPL	18.9	8.2	7.0	34.1
MoCo-TC2	400	1-MN	SSL	32.4	18.0	24.2	74.6
MoCo-TC2	400	1-MN	TPL	37.0	19.8	22.0	78.7
None	425	1-MN	SSL	16.7	16.4	13.8	46.9
MoCo-TC2	425	1-MN	SSL	42.3	14.9	14.8	72.0
MoCo-TC2	425	1-MN	TPL	46.7	19.5	15.0	81.1
MoCo-TC3	425	1-MN	SSL	36.7	11.9	13.2	61.4
MoCo-TC3	425	1-MN	TPL	46.3	17.5	12.9	76.6
None	400	Tetralin	SSL	29.4	20.6	21.4	71.4
None	400	Tetralin	TPL	34.4	21.1	23.7	79.2
MoCo-TC2	400	Tetralin	SSL	44.1	22.9	21.0	88.1
MoCo-TC2	400	Tetralin	TPL	46.4	25.4	17.4	89.2
DECS-12 Pittsburgh #8 Bitum Coal							
None	400	1-MN	SSL	13.7	20.4	26.8	60.9
MoCo-TC2	400	1-MN	SSL	14.5	27.8	34.3	76.6
MoCo-TC2	400	1-MN	TPL	15.8	28.7	35.4	79.9
None	425	1-MN	SSL	16.3	17.6	16.1	51.4
MoCo-TC2	425	1-MN	SSL	21.8	27.6	23.9	73.3
MoCo-TC2	425	1-MN	TPL	33.1	31.5	23.4	87.9
MoCo-TC2	400	Tetralin	SSL	18.8	32.6	31.0	82.4
MoCo-TC2	400	Tetralin	TPL	21.9	34.2	33.0	89.1

** Impregnated from toluene solution using incipient wetness method.

In regard to the catalytic effects associated with solvent, the increases in conversion and oil yield due to catalyst are much higher when using a non-donor 1-MN solvent as compared to the runs using a H-donor tetralin (Table 12). For example, for SSL runs of DECS-9 coal at 400°C, using MoCo-TC2 increased coal conversion from about 32 to 75 wt% $[(75-32)/32 = 134\% \text{ increase}]$ with 1-MN, and from about 71 to 88 wt% $[(88-71)/71 = 24\% \text{ increase}]$ with tetralin. In the presence of H-donor solvent, the catalytic effects relative to thermal runs appear to be higher in SSL runs than under TPL conditions, as can be seen by comparing the thermal and catalytic runs with tetralin in Table 12.

Conclusions

This work provides a fundamental approach to developing novel bimetallic dispersed catalysts and optimum conditions for coal conversion. We have synthesized and tested several heterometallic complexes consisting of two transition metals [Co, Mo] and sulfur as precursors of bimetallic dispersed catalysts for liquefaction of a subbituminous and a bituminous coal. The results revealed that both the ligands to the metal species and the type of bonding between the two metals affect the activity of the resulting catalyst significantly. Among the M-M'' type precursors tested, Mo-Co thiocubane cluster, $\text{Mo}_2\text{Co}_2\text{S}_4(\text{Cp})_2(\text{CO})_2$ [MoCo-TC2], produced the best catalyst. Loading of MoCo-TC2 at the level of 0.5 wt% Mo can increase the conversion of the subbituminous coal from 32 to as high as 80 wt%. The performance of the Mo-Co bimetallic catalyst was further enhanced by using temperature programmed heat-up (TPL) conditions. For a final temperature of 425°C, using the programmed conditions with MoCo-TC2 significantly increased the conversions by about 12-13 wt% for both coals, as compared to the non-programmed runs. Further work is now in progress.

References

- Brunner, H.; Wachter, J., *J. Organomet. Chem.* 1982, 240, C41-44.
- Derbyshire, F.J.; *Catalysis in Coal Liquefaction*, IEACR/08, IEA Coal Research, London, 1988, 69 pp.
- Garg, D.; Givens, E.N.; *Fuel Process. Technol.*, 1984, 8, 123-134.
- Halbert, T. R.; Cohen, S. A.; Stieffel, E. I., *Organometallics* 1985, 4, 1689-1690.
- Halbert, T.R.; Ho, T. C. Stieffel, E. I.; Chianelli, R. R., Daage, M., *J. Catal.* 1991, 130, 116-119.
- Herrick, D. E.; Tierney, J. W.; Wender, I.; Huffamn, G. P.; Huggins, F. E., *Energy & Fuels* 1990, 4, 231-236,

- Hirschon, A.S.; Wilson, R.B.; Am. Chem. Soc. Sym. Ser., 1991, 461, 273-283.
- Hirschon, A.S.; Wilson, R.B.; Fuel, 1992, 71, 1025-1031.
- Huang, L.; Song, C.; Schobert, H. H., Am. Chem. Soc. Div. Fuel Chem. Prepr., 1992, 37(1), 223-227.
- Mingos, D.M.P.; Wales, D.J., "Introduction to Cluster Chemistry", Prentice Hall: Englewood Cliffs, New Jersey, 1990, 318 pp.
- Solar, J.M.; Derbyshire, F.J.; de Beer, V.H.J.; Radovic, L.R.; J. Catal., 1991, 129, 330-342.
- Sommerfeld, D.A.; Jaturapitpornsakul, J.; Anderson, L.; Eyring, E.M.; Am. Chem. Soc. Div. Fuel Chem. Prepr., 1992, 37(2), 749-755.
- Song, C.; Nomura, M.; Miyake, M.; Fuel, 1986, 65, 922-926.
- Song, C.; Hanaoka, K.; Nomura, M.; Fuel, 1989, 68, 287-292.
- Song, C.; Nomura, M.; Ono, T., Am. Chem. Soc. Div. Fuel. Chem. Prepr. 1991, 36(2), 586-596.
- Song, C.; Schobert, H. H.; Hatcher, P. G., Energy & Fuels, 1992, 6, 326-328.
- Song, C.; Schobert, H. H.; Am. Chem. Soc. Div. Fuel. Chem. Prepr. 1992, 37(2), 976-983.
- Suzuki, T.; Ando, T.; Watanabe, Y., Energy & Fuels 1987, 1, 299-300.
- Swanson, A.; Am. Chem. Soc. Div. Fuel. Chem. Prepr. 1992, 37(1), 149-155.
- Yamada, O.; Suzuki, T.; Then, J.; Ando, T.; Watanabe, Y.; Fuel Process. Technol., 1985, 11, 297-311.

APPENDIX A-1
FIGURES

Figure 1. The disappearance of the substrate compounds with reaction time at 450°C

Figure 2. Bonding energies of α and β bonds in butylbenzenes at 450°C

Figure 3. The formation of solid products versus reaction time at 450 °C from the pyrolysis of butylbenzenes.

(a) benzene

(b) toluene

(c) ethylbenzene

(d) n-propylbenzene

(e) isopropylbenzene

Figure 4. Selectivities of some cracking products.

Figure 5. Isomerization reactions during the pyrolysis of n-BB and t-BB

Figure 6. Temporal variation of the molar yields of naphthalene in the pyrolysis of butylbenzenes

Figure 7. Carbon deposits collected on the reactor surface with/without metal grids (450°C, 5 hr., 5 ml n-dodecane).

Figure 8. Carbon deposits collected on the reactor walls with/without metal grids (450°C, 5 hr., 5 ml dodecane).

Figure 9. Carbon deposit collected on the reactor surface with/without metal grids (450 °C, 5 hr., 5 ml Jet A fuel).

Figure 10. Carbon deposit collected on the reactor walls in the presence of metal wires (450°C, 5 hr., 5 ml dodecane).

Figure 11. Carbon deposit collected on the reactor walls in the presence of metal wires (450°C 5 hr., 5 ml Jet A fuel).

Figure 12. SEM micro graphs of the deposit on metal grids: (a) Cu grid; (b) Ni grid; (c) S.S grid; (d). Ti grid; (e) Au grid.

Figure 13. Three types of growth pattern of carbon deposit in thermal stressing of dodecane (450 C, 5 hr): (a) perpendicular (Au & SS grids); (b) lateral (Ni & Ti grids); (c) perpendicular-lateral combined (Cu grids).

a

b

c

d

e

Figure 14. SEM micro graphs of the deposits on metal grids: (a) Ni grid; (b) Cu grid; (c) S.S. grid; (d) Ti grid; (e) Au grid.

Figure 15. Size distribution of insoluble particles suspended in coal-derived jet fuel after treatment for 6 hours at 450°C in the presence of nitrogen. The size distribution was measured using laser diffraction (Malvern droplet and particle sizer) several days after cooling the reactor.

Figure 16. Top: formation of solid deposit, and bottom: concentration of suspended particles, as functions of the mass fraction of tetradecane added to coal-derived jet fuel. Steeping was for 6 hours at 450°C in the presence of nitrogen.

Figure 17. Variation of the color of carbon deposit along the flow-reactor tube (Jet Fuel, Ram 92004.001).

Figure 18. Polarized-light micrographs of deposit obtained from thermal stressing of JP8 jet fuel alone.

100 μm

Figure 19. Polarized-light micrographs of deposit obtained from thermal stressing of JP8 jet fuel in the presence of alumina.

100 μm

Figure 20. Polarized-light micrographs of deposit obtained from thermal stressing of JP8 jet fuel in the presence of original deposit.

Figure 21a. Gas chromatogram of the liquid product from JP9 neat stressed at 450°C for 1 h.

Figure 21b. Gas chromatogram of the liquid product from JP8 neat + activated carbon stressed at 450°C for 1 h.

Figure 22. Percent peak areas versus alkane carbon number in the original jet fuel and the stressed products.

Figure 23. Product yield versus alkane carbon number for the stressed liquids.

- JP8, 450°C, 0.5h.
- JP8+AC, 450°C, 0.5h.
- JP8, 450°C, 1h.
- JP8+AC, 450°C, 1h.

Figure 24. Alkane carbon number versus alkane/alkylbenzene ratio in the stressed products.

- JP8, 450°C, 0.5h.
- JP8+AC, 450°C, 0.5h.
- JP8, 450°C, 1h.
- JP8+AC, 450°C, 1h.

Figure 25. Alkane/naphthalene ratio versus alkane carbon number in the stressed products.

Figure 26. Percent peak areas plotted versus the number of alkyl groups on benzene.

Figure 27. Percent peak areas plotted versus alkane carbon numbers for the stressed products.

Figure 28. ^{13}C NMR spectra of thermally stressed Jet A-1 with 0.25 mL of 100% labeled α - ^{13}C -benzyl alcohol plus 0.25 mL of unlabeled benzyl alcohol. (a) benzyl alcohol; (b) toluene; (c) benzaldehyde; (d) benzoic acid; (3); (*) chloroform.

Figure 29. Mass spectrum of toluene at 720 minutes.

Figure 30. Coal conversion vs. percent hydrogen transfer @ 730°F.³

Figure 31. Coal conversion vs. percent hydrogen transfer @ 670°F.³

Figure 32. Conversion of coal in benzylic and hydroaromatic radical scavengers. At equal levels of available hydrogen in methyl--naphthalene solution, 400°C.²⁵

Figure 33. ^{13}C NMR for Blind Canyon.

Figure 34. ^{13}C NMR for Pittsburgh 8.

Figure 36. Flash Pyrolysis GC/MS Blind Canyon Residue.

Figure 37. Flash Pyrolysis GC/MS Blind Canyon Residue.

Figure 38. Flash Pyrolysis GC/MS Pittsburgh 8.

Figure 39. Flash Pyrolysis GC/MS Pittsburgh #8 Residue.

Figure 40. GC/MS for hexane solubles.

Figure 41. GC/MS for light distillate Blind Canyon.

Figure 42. GC/MS for light distillate Pittsburgh 8.

Figure 43. Coal liquefaction conversion data for Blind Canyon and Pittsburgh 8 coals.

Figure 44. GC/MS of hydrogenated rosin at 350°C.

Figure 45. GC/MS of hydrogenated rosin at 400°C.

Figure 46. GC/MS of hydrogenated rosin at 45°C.

Figure 47. GC/MS of hydrogenated rosin at 500°C.

Figure 48. Plot to show product distribution vs temperature.

Figure 49. GC/MS of hydrogenated rosins at 450°C for 5 minutes.

Figure 50. GC/MS of hydrogenated rosins at 450°C for 20 minutes.

Figure 51. GC/MS of hydrogenated resins at 450°C for 30 minutes.

Figure 52. GC/MS of hydrogenated rosins at 450°C for 60 minutes.

Figure 53. Plot to show product distribution vs time at 450°.

Figure 54. Hydrogenation reaction pathway of abietic acid in rosin.

MAJOR CRACKING PRODUCTS

+

OTHER ALKYL BENZENES & SUBSTITUTED NAPHTHALENES

Figure 55. Cracking reaction pathway of abietic acid in rosin.

APPENDIX A-2
TABLES

Table A. Products from Pyrolysis of 5 mL of n-C14 at 450°C under 0.69 MPa N₂ (Cold) in 25 mL microautoclave (**average of two runs for GC data).

Residence time Expt No.	Reactor Residence Time in Sandbath Preheated to 450°C ^a							
	6 min	12 min	21 min	30 min	60 min	150 min	240 min	480 min
	TS84	TS83	TS82	TS85/86	TS45	TS62	TS67**	TS75
Yields (mol %)^b								
Hydrogen (H ₂)	0	0	0	1.17	3.21	4.67	8.09	8.43
Methane (C ₁)	0.45	1.73	3.90	8.33	21.63	34.93	70.31	73.48
Ethane (C ₂)	1.04	3.53	6.78	13.76	29.01	49.44	74.48	84.05
Ethylene	0.37	1.06	1.62	2.21	4.37	2.36	2.38	2.69
Propane (C ₃)	0.83	1.95	3.58	7.08	18.94	37.25	46.93	57.54
Propylene	0.49	1.57	2.70	5.20	10.01	12.69	10.52	11.23
iso-Butane	0	0	0	0.03	0.26	0.88	1.45	1.97
n-Butane [§]	0.15	0.46	0.84	1.75	5.49	12.71	15.10	17.66
n-Butane ^L	0.20	1.56	3.47	6.66	2.00	3.47	2.52	3.42
1-Butene [§]	0.12	0.38	0.63	1.02	2.41	3.55	2.43	2.06
1-Butene ^L	0.27	1.35	3.00	5.72	1.22	1.04	0.40	0.34
n-Butane (n-C ₄) ^{sum##}	0.35	2.02	4.31	8.41	7.49	16.18	17.62	21.08
1-Butene ^{sum##}	0.39	1.73	3.63	6.74	3.63	4.59	2.83	2.40
Pentane (n-C ₅)	0.16	1.17	3.15	7.00	10.00	16.45	14.71	13.76
1-Pentene	0.41	2.13	3.36	5.71	5.08	6.32	2.45	1.25
n-Hexane (n-C ₆)	0.23	1.21	2.75	5.67	10.38	12.23	12.65	11.75
1-Hexene	0.40	2.10	3.20	4.96	3.99	3.16	2.70	1.17
n-Heptane (n-C ₇)	0.24	1.28	2.70	5.15	9.63	9.60	9.21	7.38
1-Heptene	0.35	1.61	2.50	3.35	3.74	3.83	2.36	2.95
n-Octane (n-C ₈)	0.21	1.13	2.36	4.44	7.59	7.62	6.99	4.35
1-Octene	0.31	1.36	1.95	2.61	2.02	0.24	0.06	0
n-Nonane (n-C ₉)	0.21	1.04	2.11	3.66	6.34	5.82	4.93	2.53
1-Nonene	0.31	1.23	1.77	2.31	0.59	0.22	0.09	0
n-Decane (n-C ₁₀)	0.19	0.92	1.82	2.94	4.85	4.50	3.25	1.64
1-Decene	0.29	1.13	1.53	1.47	1.05	0.27	0.03	0
n-Undecane (n-C ₁₁)	0.20	0.93	1.76	2.69	4.04	3.54	2.30	1.05
1-Undecene	0.27	1.00	1.32	1.27	0.67	0	0	0
n-Dodecane (n-C ₁₂)	0.03	0.19	0.45	0.82	1.37	1.04	0.81	0.36
1-Dodecene	0.27	0.97	1.28	1.17	0.31	0.05	0	0
n-Tridecane (n-C ₁₃)	0.02	0.09	0.26	0.51	0.78	0.58	0.40	0.20
1-Tridecene	0.06	0.22	0.32	0.25	0.06	0	0	0
n-Tetradecane (n-C ₁₄)	96.02	83.08	68.32	46.67	29.73	9.37	2.92	0.84
1-Tetradecene	0	0.02	0.14	0.21	0	0	0	0
n-Pentadecane (n-C ₁₅)	0.08	0.14	0.24	0.36	0.42	0.23	0	0
n-Hexadecane (n-C ₁₆)	0	0.06	0.16	0.26	0.29	0.12	0.06	0
n-Heptadecane (n-C ₁₇)	0	0.04	0.11	0.17	0.16	0.04	0	0
n-Octadecane (n-C ₁₈)	0.13	0.13	0.15	0.18	0.13	0.01	0	0
n-Nonadecane (n-C ₁₉)	0	0.02	0.07	0.09	0	0	0	0
n-Eicosane (n-C ₂₀)	0	0.02	0.06	0.07	0	0	0	0
n-Henicosane (n-C ₂₁)	0	0.02	0.04	0.05	0	0	0	0
n-Docosane (n-C ₂₂)	0	0.01	0.03	0.04	0	0	0	0
n-Tricosane (n-C ₂₃)	0	0.01	0.02	0.03	0	0	0	0
Alkylcyclopentanes	0	0.06	0.20	0.69	3.40	3.43	3.52	5.01
Alkylcyclohexanes	0	0.13	0.57	1.71	5.68	6.80	5.62	5.53
Alkylbenzenes	0	0	0	0.44	4.50	14.48	21.39	23.35
Tetralins	0	0	0	0	0	0	0.04	0.13
Indanes	0	0	0	0	0	1.45	2.64	2.94
Alkylnaphthalenes	0	0	0	0	0	1.57	2.95	4.16
Other Polyaromatics	0	0	0	0	0	0.03	0.24	0.47
Solids (wt% of C14)	0	0	0	0	0	1.0	3.0	4.7

a) The reactors reach 450°C in about 3 minutes after plunge into the sandbath.

b) The molar yield based on n-tetradecane substrate.

Table B. Products from H-transferring pyrolysis of 5 mL of tetradecane-tetralin mixture at 450°C under 0.69 MPa N₂ (cold) in 25 mL microautoclave.

Residence time vol% of Tetralin	Reactor Residence Time in Sandbath Preheated to 450°C ^a										
	6 min 10%-THN	12 min 10%-THN	21 min 10%-THN	30 min 10%-THN	30 min 100%THN	240 min 5 % THN	240 min 10%-THN	240 min 15 % THN	240 min 25 % THN	240 min 50 % THN	240 min 100 % THN
Expt No.	MTS32	MTS31	MTS30	MTS26	TS79	MTS14	MTS20	MTS24	MTS21	MTS7	TS6
Yields (mol %)^b											
Hydrogen (H ₂)					0.73						
Methane (C ₁)	0.38	0.59	0.98	2.39	0.01	87.29	45.85	40.43	28.06	23.77	0.41
Ethane (C ₂)	1.01	1.43	2.21	4.55	0.07	84.18	56.05	50.74	37.40	29.93	0.21
Ethylene	0.22	0.40	0.55	0.76	0	1.75	1.41	0.60	1.11	0.50	0.01
Propane (C ₃)	0.60	0.78	1.22	2.51	0.02	44.10	38.24	37.01	26.86	19.14	0.27
Propylene	0.41	0.64	1.07	2.08	0.04	10.11	6.40	9.03	8.21	5.73	0.06
iso-Butane	0.02				0.01	0.66	0.92	0.96	0.42	0.20	0.09
n-Butane ^f	0.14	0.19	0.30	0.60	0.02	11.20	13.46	12.72	9.01	6.16	0.23
n-Butane ^L	0.17	0.30	1.01	4.66			10.76		11.49		
1-Butene ^f	0.08	0.14	0.23	0.38	0	2.23	1.77	2.24	2.10	1.56	0.03
1-Butene ^L	0.17	0.49	1.04	3.17			1.20		1.27		
n-Butane (n-C ₄) ^{sum##}	0.31	0.49	1.31	5.26			24.22		20.5		
1-Butene ^{sum##}	0.34	0.63	1.27	3.55			2.97		3.37		
Pentane (n-C ₅)	0.13	0.35	0.73	5.48			17.70		20.06		
1-Pentene	0.28	0.69	1.28	4.99			1.27		5.02		
n-Hexane (n-C ₆)	0.18	0.43	0.84	4.82			14.36		18.09		
1-Hexene	0.25	0.60	1.16	3.76			1.36		1.59		
n-Heptane (n-C ₇)	0.20	0.44	0.93	2.27			10.62		9.51		
1-Heptene	0.22	0.50	1.01	3.34			2.03		3.00		
n-Octane (n-C ₈)	0.18	0.39	0.83	2.66			7.95		7.05		
1-Octene	0.22	0.47	0.90	2.24			?		?		
n-Nonane (n-C ₉)	0.16	0.37	0.80	2.40			5.21		5.28		
1-Nonene	0.21	0.44	0.85	1.73			0.14		0.17		
n-Decane (n-C ₁₀)	0.15	0.34	0.73	2.05			3.70		3.90		
1-Decene	0.21	0.43	0.80	1.46			0		0		
n-Undecane (n-C ₁₁)	0.16	0.35	0.75	1.96			2.72		3.05		
1-Undecene	0.19	0.39	0.72	1.23			0		0		
n-Dodecane (n-C ₁₂)	0.03	0.04	0.13	0.44			0.85		0.89		
1-Dodecene	0.18	0.37	0.70	1.15			0		0		
n-Tridecane (n-C ₁₃)	0	0.01	0.05	0.21			0.40		0.38		
1-Tridecene	0.05	0.10	0.17	0.26			0		0		
n-Tetradecane (n-C ₁₄)	97.36	94.61	89.16	66.24			4.52		8.02		
1-Tetradecene	0	0	0	0							
n-Pentadecane (n-C ₁₅)	0.09	0.09	0.10	0.18			0.05		0.15		
n-Hexadecane (n-C ₁₆)	0	0	0.02	0.09			0.22		0.02		
n-Heptadecane (n-C ₁₇)	0	0	0	0.08			0.02		0.04		
n-Octadecane (n-C ₁₈)	0.13	0.13	0.13	0.13			0.03		0		
n-Nonadecane (n-C ₁₉)				0.05			0		0		
n-Eicosane (n-C ₂₀)				0.06			0		0		
n-Henicosane (n-C ₂₁)				0.03			0		0		
n-Docosane (n-C ₂₂)				0.02			0		0		
n-Tricosane (n-C ₂₃)				0.02			0		0		
Alkylcyclopentanes				0.24							
Alkylcyclohexanes				0.49							
Alkylbenzenes	0	0	0	0.29							
Tetralins				83.03							
Indanes				5.06							
Alkyl naphthalenes	0.68	0.83	1.36	8.41							
Other Polyaromatics											

a) The reactors reach 450°C in about 3 minutes after plunge into the sandbath.

b) The molar yield based on n-tetradecane substrate.

Table C. Yield and opposition of liquid obtained after stressing of JP8 alone and in the presence of different carbons.

ADDED CARBON	LIQUID YIELD		LIQUID COMPOSITION					
	ML,	ML,	$\frac{AL}{AR}$	$\frac{AL}{AR}$	$\frac{C11}{C11}$	$\frac{C11}{C11}$	$\frac{C11}{C11}$	$\frac{C11}{C11}$
	5 HRS.	1 HR.	5 HRS.	1HR.	5 HRS.	1 HR.	5 HRS.	1 HR.
ACTIVATED CARBON	3.5	4.9	0.89	1.77	2.28	4.45	68.40	0
CARBON BLACK	4.5	-	1.05	-	1.20	-	16.88	-
SP1 GRAPHITE	3.8	-	0.83	-	1.47	-	30.63	-
ALUMINA	4.0	-	0.96	-	2.12	-	122.00	-
DEPOSIT	5.0	-	1.14	-	1.40	-	20.60	-
NONE	5.2	6.5	1.35	2.17	1.42	5.69	22.27	0

Table D. Yield and composition of gases obtained after thermal stressing of JP8 jet fuel alone and in the presence of different solid carbons.

ADDED CARBON	GAS YIELD		GAS COMPOSITION			
	ML, 5 HRS.	ML, 1 HR.	$\frac{\text{CH}_4}{\text{C}_3\text{H}_8}$ 5 HRS.	$\frac{\text{CH}_4}{\text{C}_3\text{H}_8}$ 1 HR.	$\frac{\text{C}_1}{\text{C}_4}$ 5 HRS.	$\frac{\text{C}_1}{\text{C}_4}$ 1 HR.
ACTIVATED CARBON	784	796	0.21	0.76	0.45	1.51
CARBON BLACK	650	-	1.61	-	3.36	-
SP1 GRAPHITE	636	-	0.68	-	1.32	-
ALUMINA	806	-	0.63	-	1.19	-
DEPOSIT	545	-	0.88	-	1.56	-
NONE	662	637	2.12	2.12	4.95	0.86

END

**DATE
FILMED
8/19/93**