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ADVANCED THERMALLY STABLE JET FUELS

Technical Progress Report
November 1992 – January 1993

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

Contributions from:

R. Arumugam, J. Bortiatynski, R. Dutta, K. Gergova, L. Hou, W-C. Lai, J. Li,
D. McKinney, Y. Peng, P. Sanghani, L. Selvaraj, M. Sobkowiak

March 1993

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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 octylbenzene was studied at 400°, 425°, and 450°C. There are some general features of similarity between the reactions of octylbenzene and those of the butylbenzenes reported in the previous Technical Progress Report (92PC92104-TPR-1, February 1993). For example, both produce a large amount of smaller alkylbenzenes during pyrolysis. Reaction kinetics of octylbenzene were calculated, and the major chemical pathways in its thermal reactions were determined.

Pyrolysis of tetradecane was studied at 450° at pressures of 2–9 MPa and reaction times of 6–480 min. The major products in the initial stage of reaction are C₁–C₁₁ n-alkanes and C₂–C₁₂ 1-alkenes. There are very little paraffinic products with 12 or 13 carbon atoms. Formation of alkenes with 13 carbon atoms is very limited, but 1-dodecene is as abundant as the C₂–C₁₁ 1-alkenes. As compared to gas-phase pyrolysis, the alkene/alkane molar ratios are much smaller, except for the C₁₂ group, where the ratio of 1-dodecene/dodecane can be as high as 9 in the initial stage. This is because the terminal alkene is produced from β -scission of a secondary radical, whereas the alkane is formed from a primary radical whose population is much lower than the secondary radical, due both to higher activation energy and to competing isomerization reactions. 1-Hexene and 1-pentene appeared to be formed preferentially among the alkenes after 12 min. This may be attributed to 1,4- and 1,5-shift isomerization of primary radicals. The peak of carbon number distribution shifts towards 2 for paraffinic products and towards 3 for olefinic products, and the ratios of alkenes to alkanes decrease with increasing residence time up to 60 min. Alkane molecules are the source for hydrogen abstraction in the initial periods, but in the later stages the olefinic products also undergo H-abstraction reactions which lead to the formation of cyclohexanes,

cyclopentanes, and alkylaromatics. The alkylaromatics include mainly alkylbenzenes, together with smaller amounts of alkyl-substituted indanes and naphthalenes.

The chemical composition of a metal surface, as well as of the starting materials, has a significant effect on carbon deposit formation during thermal stressing of Jet A and dodecane (Technical Progress Report 92PC92104-TPR-1, February 1993). Transmission electron microscope grids were placed at the top and bottom of reactors before thermal stressing of Jet A and dodecane to study the deposition processes at these positions. The motivation for this work was to obtain information on the phases existing during thermal stressing inside a microautoclave, deduced from observed microstructures of the carbonaceous solid. Optical textures and morphologies of carbonaceous deposits generated on reactor walls and on metal grid surfaces from Jet A and dodecane at 450° for 1, 3, and 5 hours were examined using polarized light optical microscopy and scanning electron microscopy. The metal grid / deposit interface was also examined. In addition, the effect of surface roughness on deposit formation was also studied, since the grids inherently contain smooth and rough surfaces.

Evidence from previous work with coal-derived jet fuel (JP-8C) suggested that solid deposits were formed on the vertical surfaces of the static microautoclave reactor by direct addition of reactive species to the wall from the fluid, but that deposits on the bottom of the reactor formed by gravitational settling of particles formed in suspension. The experiment was modified to enable a quantitative comparison of settling and deposition rates.

Different solid carbons were added to JP-8 to investigate the effects of carbon surfaces on solid deposition and on the chemistry of thermal degradation. Thermal stressing was conducted at 450°C for 5 hours in the presence of two different activated carbons, carbon black, graphite, alumina, and carbon deposits recovered from previous reactions. A clear difference in the appearance of liquid products was observed only with addition of 1 g activated carbon to 10 mL of JP-8, the liquid after stressing being much lighter in color than liquid from JP-8 stressed without additive. All the added solid carbons appear to have a substantial influence on the deposition process. Some (activated carbons, carbon black, and graphite) prevent deposition at these conditions, while the others (alumina and deposits recovered from previous stressing) provide more attractive areas for deposition than the 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. Deposition mechanisms are also affected by the presence of different carbon surfaces during thermal stressing. The solid carbons with the most disordered structure and highest surface reactivity (i.e., activated carbons) produced the most significant effect on thermal degradation. These surfaces appear to be effective in stabilizing free radicals or enhancing

recombination reactions. It is not yet clear whether the surface area or the pore size distribution of the activated carbons is responsible for preventing solid deposition and stabilizing the fuel.

It was decided to simplify the experimental methodology of fuel stabilization studies to elucidate the underlying mechanisms involved. Understanding the reasons why benzyl alcohol and similar molecules retard the formation of carbonaceous solids in hydrocarbon mixtures at high temperature is important and should point the way to the design of superior additives in the future. Typical jet fuels are highly complex mixtures, which make the analysis of the products of thermal degradation in the presence of additives very complicated. Dodecane was chosen as a model compound for additive studies since it is the most abundant hydrocarbon in jet fuels, and numerous other studies have been performed on dodecane.

Hydrogen transferring pyrolysis—thermal decomposition of hydrocarbons in the presence of hydrogen donors—was investigated as a method for enhancing high-temperature stability. Relative to the pyrolysis of pure tetradecane at 450°C, adding 10 vol.% of the hydrogen donor tetralin suppressed decomposition by about 68% after 11 min., 66% after 21 min., and 37% after 30 min. Tetralin not only inhibited the decomposition, but also altered the product distribution. Decomposition and isomerization of primary radicals are strongly suppressed, leading to a much higher ratio of 1-dodecene to dodecane and slightly higher alkene/alkane ratios for the other product groups. The overall reaction mechanism for the initial pyrolysis stage is characterized by a one-step β -scission of a secondary radical followed by H-abstraction of the resulting primary radical. Desirable effects of hydrogen donor addition are also observed even after 240 min. at 450°C, especially for inhibiting solid deposition. Adding 10 vol% tetralin to JP-8, tetradecane, and n-butylbenzene reduced the formation of deposits by 90%, 77%, and 54%, respectively.

Coals rich in resinite are considered potential feedstocks for jet fuel production, since resins consist predominantly of two-ring cycloalkane structures. These cycloalkanes are linked to the side chains of these coals networks and can be liberated in liquefaction processes. To optimize the liquefaction process, an adequate understanding of the structures of potential coal feedstocks is a necessary task. Various NMR parameters have been obtained for two samples of Blind Canyon (Utah) bituminous coal using solid state ^{13}C NMR. The experiments included cross-polarization and magic-angle spinning, Bloch decay, dipolar dephasing and various relaxation time experiments.

If the behavior of resinite under liquefaction conditions can be determined and understood, a highly efficient liquefaction system can be developed. Coals with high resinite concentration can be liquefied, and the cycloparaffinic products from resinite can be extracted into the oil fraction producing liquids that are thermally stable and could be a

source of high quality jet fuel. However, because resinite is a complex mixture of polymerized products, it is helpful 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 analog of resinite and its hydrogenation and dehydrogenation behavior should give an insight into resinite liquefaction. Diterpenoid compounds can in fact be successfully hydrogenated and cracked to jet fuel components using nickel-molybdenum (on alumina) and nickel Y-zeolite catalysts.

Several heterometallic complexes consisting of molybdenum, cobalt, and sulfur in a single molecule were synthesized and tested as precursors of dispersed catalysts for liquefaction of Montana subbituminous coal. Both the nature of the ligands to the metal species and the type of bonding between the two metals significantly affect the activity of the catalyst generated in situ. Among the precursors tested, Mo-Co thiocubane, $\text{Mo}_2\text{Co}_2\text{S}_4\text{Cp}_2(\text{CO})_2$ (where Cp is cyclopentadiene) produced the best catalyst.

TECHNICAL PROGRESS

Task 1. Investigation of the Quantitative Degradation Chemistry of Fuels

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

Introduction

The pyrolysis of octylbenzene (OB) at various temperatures, 400°C, 425°C and 450°C, has been studied. This work represents a continuous effort in the study of the effects of alkylbenzenes in the high temperature thermal degradation of jet fuels, following up the detailed study of the behavior of four isomers of butylbenzenes (1). There are some general similarities in the reactions of OB and butylbenzenes. For example, both produce a large amount of smaller alkylbenzenes during pyrolysis.

Reaction kinetics of OB have been calculated based on the temperature range mentioned above, and the major chemical process in its thermal reactions have been analyzed. The experimental apparatus and the analytical procedure employed are identical to those reported in the last quarterly report (1) and will not be described here.

Thermal Stressing of OB under Temperatures 400°C, 425°C and 450°C

As expected, temperature plays the most significant role in the degradation process, as shown in Figure 1. The reaction shows only a moderate rate at 400°C, 8.18 mol% of OB remaining after 16 hours of stressing. At 450°C, however, there is virtually no OB left after 8 hours of stressing. Rough comparison of the yields (wt%) of gaseous, liquid and solid products formed (Figures 2, 3 and 4) shows a uniform change in this temperature range. For example, a steady increase of the yields (wt%) of gas and solid formation can be observed in Figures 2 and 3.

Reaction Kinetics of Octylbenzene

Global kinetics of the reaction of octylbenzene have been calculated according to the following steps:

The rate of disappearance of octylbenzene in the stressing can be expressed generally in equation [1], where C_A is the concentration of octylbenzene (mol%) at time t (hour), k is the reaction rate constant, the unit of which depends on the reaction order.

$$-dC_A / dt = k C_A^n \quad [1]$$

Concentration of OB at time t can also be expressed in terms of its initial concentration C_{A0} and its conversion X at time t as shown in equation [2]:

$$C_A = C_{A0} (1-X) \quad [2]$$

Combining equations [1] and [2], equation [3] can be obtained:

$$dX / dt = k C_{A0}^{n-1} (1-X)^n \quad [3]$$

If we plot $\log (dX / dt)$ versus $\log (1-X)$, a straight line with a slope of reaction order n and intercept of kC_{A0}^{n-1} can be obtained. Figure 5 shows the plot in the temperature range of interest.

It can be seen from the equations or Figure 5 that the reaction order varies from 0.835 at 450°C to 1.219 at 400°C. At the temperature of the reaction increases, the reaction order decreases. Roughly, however, the reaction order can be assumed to be about 1. The physical meaning of a reaction order 1 is unimolecular decomposition. This implies that the major pathway of octylbenzene decomposition is through its thermal breakdown to form benzyl radicals and *n*-heptyl radicals. This dissociation process has been generally accepted and can be verified by GC and GC-MS analysis of gaseous and liquid products, as will be shown in the latter part of this section. The increasing trend of reaction order with the decreasing of reaction temperature may indicate that bimolecular reactions are gradually enhanced as temperature decreases. It should be noted that a decrease in temperature lowers the reaction pressure and, therefore, the chance for bimolecular reaction. It can be inferred that in this respect the temperature effect is dominant relative to a pressure effect. From the intercept of Figure 5, global reaction rate constants ($k' = k C_{A0}^{n-1}$) can also be obtained. Figure 6 shows the Arrhenius plot of the global behavior of octylbenzene based on the first order reaction assumption. An activation energy value (E_a) of 39.56 kcal/mol and preexponential factor (A) of $2.664 \times 10^{12} \text{ hr}^{-1}$ can be achieved. It should be pointed out that the E_a value obtained is significantly less than the C_α - C_β dissociation energy in the side chain of octylbenzene. The participation of secondary reactions, such as H-abstraction, in the consumption of OB may be one of the reasons for the reduction of the global activation energy. Under the reaction conditions used in this work, a high N_2 overpressure greatly facilitates the reactions between OB and other radicals (e.g., $H\bullet$, $CH_3\bullet$). The net effect of these two-body reactions, which have low E_a , is to greatly decrease the overall E_a value.

Liquid Product Analysis

Table 1 displays the major products and their amounts in liquid products after 1, 4 and 8 hours of stressing. After 1 hour at 400°C, major products are hexane, 1-heptene, toluene and styrene. As reaction time is prolonged, toluene and hexane increase, whereas heptene and styrene diminish rapidly. The general picture of liquid product formation and their changing patterns with time appears to be similar to the butylbenzenes, except that as the length of the chain increases, greater amounts of smaller products, such as pentane, pentene and hexane, are formed. They are obviously not observed in the liquid products of the four butylbenzenes. A detailed mechanism will be given in a future report.

References

- (1) H.H. Schobert, S. Eser, C. Song, P.G. Hatcher, P.M. Walsh and M.M. Coleman, Advanced Thermally Stable Jet Fuels, Technical Progress report, August 1992-October 1992, Prepared for U.S. Department of Energy under Contract No. DE-FG22-92PC92104.

2. Pyrolysis of Tetradecane at Elevated Pressure for Long Duration: Product Distribution and Reaction Mechanisms (Contributed by Chunshan Song and Wei-Chuan Lai)

Introduction

This fundamental study was undertaken with the goals of clarifying the product distribution and the reaction mechanisms of pyrolysis of long-chain alkanes in relation to high-temperature thermal degradation of jet fuels. It is known that the concentrations of long-chain alkanes in all the commercial and military aviation jet fuels, usually within the carbon number range of C₇-C₁₇, are over 70 vol % [Martel, 1987; Song and Hatcher, 1992; Lai et al. 1992]. Knowledge of the pyrolysis of long-chain alkanes at elevated pressures for long duration will be important for developing advanced thermally stable jet fuels for future high-Mach aircraft, where fuel will serve not only as the energy source but also as the primary heat sink to cool the airframe, engine and system components, leading to high bulk-fuel temperature up to 400–500°C. Such information is also needed for understanding the behavior of paraffinic species present in petroleum and coal during their co-processing, liquefaction and upgrading in the temperature range of 400–500°C. The paraffinic nature of petroleum fuels is well known. Recently it has also been found that many of subbituminous and bituminous coals contain significant amounts of aliphatic materials [Ofosu-Asante et al., 1989]. Much of the relevant background information on the high temperature stability requirements of future jet fuels is

given in a recent paper [Song et al., 1993a]. Described below is a brief review of relevant literature on pyrolysis.

Rice [1933] and Kossiakoff and Rice [1943] are the pioneers who formulated the fundamental theory of pyrolysis. They showed that the main products of the high-temperature, low-pressure gas-phase decomposition of straight-chain alkanes are alkenes and low molecular weight alkanes, and they developed a free radical mechanism to account for the main products. Since then, the free radical mechanism has been widely accepted for pyrolytic reactions, and numerous investigations have been reported on the high-temperature, low-pressure vapor-phase pyrolysis of saturated hydrocarbons, mostly light alkanes, in relation to industrial pyrolysis processes. As Willems and Froment [1988a] indicated, the temperature range in industrial pyrolysis reactors is about 600–900 °C.

Compared to light alkanes, the pyrolysis of long-chain alkanes with carbon numbers greater than eight has received little attention, as pointed out recently by Zhou and Crynes [1986]. Voge and Good [1949] published the first paper on thermal decomposition of hexadecane at 500 °C under moderate pressures (atmospheric pressure and 2.1 MPa). Light alkenes were the primary products, and essentially no alkanes with greater than two carbon atoms were present in the products from n-hexadecane. Fabuss et al. [1964] studied the decomposition of hexadecane at high temperatures, about 600–700 °C, under pressures up to 7 MPa. They modified the free radical mechanism of Rice and Kossiakoff to account for the products formed from high-pressure gas-phase reactions at high temperatures for short residence times (0.25–10 seconds). Doue and Guiochon [1969] examined the pyrolysis of twelve C₆ to C₉ alkanes at 440–500 °C under pressures of 0.3 to 2 MPa, and discussed the radical isomerization reactions at low conversions (1–4 %). Mushrush and Hazlett [1984] performed pyrolysis of several compounds containing long unbranched alkyl groups, one of them being hexadecane. Ford [1984] studied the liquid-phase thermal decomposition of hexadecane. He found that the liquid-phase kinetics for hexadecane decomposition are very similar to the gas-phase kinetics. Zhou and Crynes [1986] and Zhou et al. [1987] reported on the thermolytic reactions of decane and mixtures of C₉–C₂₂ alkanes. More recently, Fairburn et al. [1990] pyrolyzed n-hexadecane in a microreactor under ultra-rapid pyrolysis conditions, which are characterized by rapid heating (1000 °C/s), high temperature (in excess of 700 °C) and very short residence time (< 500 ms). Such conditions, as in most previous work, are close to the conditions in industrial pyrolysis processes.

In the present study, the pyrolysis of n-tetradecane, a typical component of both commercial and military jet fuels, was conducted under conditions chosen based on the anticipated high-severity thermal requirements for advanced jet fuels in future high-Mach jet aircraft. The test temperature of 450°C (842 °F) used in this work is considered to be close to

the anticipated high bulk fuel temperature for future high-Mach aircraft [Song et al., 1993]. It has been well documented that the development of advanced jet fuels for high-Mach flights requires the testing at long residence times in fuel systems in which the fuel is subjected to moderate to high heat loads, as well as the tests under conditions of very high heat flux at short residence times which fuels encounter in their passage through fuel struts and injectors [Roquemore et al., 1989; Lee and Niedzwiecki, 1989]. Hazlett et al. [1977, 1991] studied the effects of temperature on oxidation and pyrolysis of a model jet fuel (n-dodecane) using a flow reactor, and their results apply to the short-residence time (28 seconds) degradation. The present work, however, is designed to provide fundamental knowledge on the medium- (the order of minutes) and long-duration (the order of hours) pyrolytic degradation characteristics of paraffinic jet fuels at high temperatures.

The experimental conditions used in this work are characterized by closed reactor, relatively high and continuously increasing pressure, higher density gas-phase or supercritical phases, and long residence time. Such conditions are distinctly different from those used in most previous alkane pyrolysis work (vapor phase, low pressure, flow reactor, short residence time). The reaction temperature of 450 °C in this work, though relatively high for the thermal stressing of jet fuels, is at the lower end when compared to most literature on hydrocarbon pyrolysis. In this section we will report on 1) the results of detailed analysis of products from pyrolysis of n-tetradecane (n-C₁₄) at 450°C for 6-480 min; 2) the reaction mechanisms of the pyrolysis of n-C₁₄, and the mechanisms accounting for the characteristic product distribution patterns and their changes with residence time; and 3) fate of olefinic products and formation of cyclic compounds during the long-duration pyrolysis.

Experimental

Aldrich reagent-grade normal tetradecane, CH₃(CH₂)₁₂CH₃, with purity of 99+ % (MW: 198.4; mp: -6 to -5 °C; bp: 252-254 °C; d: 0.763 g/mL) was used for all the pyrolysis experiments. Many other commercially available high-purity chemicals were used in analyzing the products. The microreactors used in pyrolysis are tubing bombs consisting of a single Swagelok port connector with two caps made of 316 stainless steel. The size of the tubing bombs is 4.0 in. long, 1.05 in. o.d., and 0.62 in. i.d.; there are connecting tubes (0.25 in. o.d.; 0.172 in. i.d.), whose total length is about 18 inches, from the reactor to the quick-connect stem and to the pressure gauge. The total volume of the reactor system is about 25 mL.

The pyrolysis was conducted at 450°C for 6-480 min under an initial pressure of 0.69 MPa UHP-N₂ (cold) in 25 mL tubing bombs using 5 mL sample. A fluidized sandbath preheated to 450°C was used as heater. The reactor pressure and temperature were monitored

immediately after the microautoclave was plunged in the sandbath. The products were separated carefully into gases, liquids, and solids. Because a batch microreactor was used and product recovery was performed very carefully, it was common to obtain a material balance of close to 100%. The reactor configuration and detailed procedure have been described elsewhere [Song et al., 1993a].

The gaseous products were analyzed by using a Perkin-Elmer AutoSystem gas chromatograph equipped with two different columns and detectors for quantifying different components. A stainless steel column (6 feet long, 1/8 inch diameter) packed with 80/100 Chemipack C18 was used to determine the hydrocarbon gases ranging from C_1 to C_6 with a flame ionization detector (FID). Another stainless steel column (10 feet long, 1/8 inch diameter) packed with 100/120 Carbosieve SII (from Supelco) was used to analyze H_2 , CO , CO_2 as well as CH_4 , C_2H_2 , C_2H_4 , and C_2H_6 with a thermal conductivity detector. The gaseous products were identified by comparing their retention time with those of standard gases from Supelco, and quantified by calibration.

The compounds in the liquid products were identified by capillary gas chromatography-mass spectrometry (GC-MS) using a Hewlett-Packard 5890 II GC coupled with HP 5971A mass selective detector operating at electron impact mode (EI, 70 eV). The column used for GC separation was a 30 m x 0.25 mm i.d. fused silica capillary column (J&W DB-17) coated with 100% phenylmethylpolysiloxane with a coating film thickness of 0.25 μm . Whenever possible, the mass spectrometric identification was further confirmed by using both the retention time and mass spectra of more than 100 pure compounds measured with the same equipment. Neat samples were analyzed in the split injection mode using the split/splitless injector. Quantification of the liquid products was accomplished by using a Perkin Elmer 8500 capillary GC equipped with FID and the same type of DB-17 column. The column temperature was programmed from 40 $^{\circ}C$ to 280 $^{\circ}C$ at a rate of 4 $^{\circ}C/min$ after a 5 min isothermal period. Some low molecular weight alkanes and alkenes, such as n-butane and 1-butene or n-pentane and 1-pentene, co-elute on the DB-17 column. For such compounds, GC-MS was used to determine their relative contribution to one single peak by selective ion monitoring of their molecular ions and characteristic fragment ions. More than 30 pure compounds were used to determine the response factors (RF) of all the major components in the liquids, which were then used to calibrate the GC peak area (A) of products. The molar yields of the products were calculated as follows.

$$Y_i \text{ (mol \%)} = \frac{RF_i \times A_i}{\sum_{i=1}^n RF_i \times A_i} \times \frac{W_{l-t} \times MW_{re}}{MW_i \times W_{re}} \times 100$$

where the subscript i denotes a reaction product; W_{l-t} is the total weight of liquid or gaseous products; W_{re} and MW_{re} are the initial weight of the reactant (n-tetradecane) and its molecular weight, respectively. Repeated tests have shown that the experimental results are at the level of 90–95 % confidence.

Results and Discussion

1. n-Tetradecane pyrolysis. The nominal residence time for pyrolysis of n-tetradecane (n-C₁₄) ranges from 6 to 480 min. For runs at relatively short residence times, it is important to know the real temperature of the reactant. Therefore, we also measured the real temperature inside the reactor by fixing a thermocouple in the middle of the tube (about 0.7 cm from the wall and 5 cm from the top or bottom of the reactor). The temperature-pressure profiles of the reactor are shown in Figure 7. For the reactor containing 5 mL n-C₁₄ under an initial N₂ pressure of 0.69 MPa, the reactant reached 95 % of the given reaction temperature in 4 min and the final temperature of $450 \pm 4^\circ\text{C}$ in 6 min. While the pressure of the reactor with only N₂ become constant after 3 min, the slope of pressure increase with n-C₁₄ dropped after 6 min. At this time the reaction temperature of 450°C and system pressure of 2.41 MPa (350 psi) are higher than the boiling point (253.5°C), critical temperature (423.7°C), and critical pressure (1.5 MPa, or 218 psi) of n-tetradecane. Therefore, liquid-phase pyrolysis, such as that of hexadecane discussed by Ford [1986], is not involved in n-C₁₄ pyrolysis reported in this section.

Figure 8 shows that after the initial heat-up, the system pressure displayed a monotonic increase with increasing residence time, which is indicative of the continuous decomposition of n-C₁₄ to form smaller compounds. The sharp pressure increase is consistent with the rapid disappearance of n-C₁₄ in the first 1 h, as also plotted in Figure 8. In the later stage the secondary decomposition reactions of the primary products also contribute to the pressure increase. In fact, pyrolysis of n-tetradecane at 450°C for 6–480 min 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. All the lighter products

contribute to building up the pressure, which also needs to be considered in designing the fuel tank for the future high-Mach aircraft.

Figure 9 shows two expanded retention time windows (1–3.9 min, 4–23 min) of some capillary chromatograms for the liquid products from *n*-tetradecane. These two windows cover the C₅–C₁₃ paraffinic and olefinic products. In the early stage of the pyrolysis, the yield of a 1-alkene in the C₅–C₁₃ range was higher than the corresponding *n*-alkane. However, the C₅–C₁₁ *n*-alkanes increase progressively and begin to override the corresponding 1-alkenes after 21 min. The products in the C₁₂ and C₁₃ groups are quite different from the others, as described below.

Table 2 shows the results of detailed product analysis, where the yields of C₁–C₂₃ as well as the cyclic hydrocarbon products are expressed as molar percentage based on the initial amount of *n*-tetradecane. From a fundamental point of view, it should be kept in mind in examining Table 2 that the system pressure is also increasing with increasing residence time; the lower pressure favors unimolecular reactions while higher pressure facilitates bimolecular reactions. There are several trends that can be seen from Table 2 and Figure 9. First, at low conversion (4 mol%), there are no particular compounds in the liquid products that have high selectivity in the carbon number range of C₅ to C₁₁. Second, the yield of *n*-C₁₂ is very low compared to any of the C₁–C₁₁ alkanes, which leads to an extremely high ratio of 1-dodecene to *n*-dodecane, especially for runs of short residence times (≤ 21 min). Even after 30 min at 450°C, 1-dodecene is still more abundant relative to *n*-C₁₂. The amounts of C₁₃ products are even smaller, especially *n*-tridecane, as can be seen clearly from Figures 8 and 9. The formation of *n*-C₁₃ becomes visible after 12 min, but it is still much less than 1-tridecene. 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 molar ratio of total amount of C₁–C₁₃ *n*-alkanes to that of C₂–C₁₃ 1-alkenes decreased as follows: 0.96 (residence time of 12 min) > 0.71 (21 min) > 0.55 (30 min) > 0.27 (60 min) > 0.17 (150 min) > 0.08 (240 min). 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.

Figure 10 shows the carbon number distribution of the C₁–C₁₃ products as mol % based on the amount of *n*-C₁₄ charged initially. Two recent papers reported the preferential formation of 1-alkenes from vapor-phase pyrolysis of long-chain alkanes [Zhou et al., 1987; Fairburn et al., 1990]. In the present work, significant amounts of alkenes, mainly 1-alkenes, were also detected, both in liquid and gaseous products. However, unlike the above-mentioned literature results for high-temperature and short-residence-time pyrolysis (very little long-chain paraffinic products), under the present conditions the C₈ to C₁₁ alkanes are

also major products. Moreover, the alkenes are not the only major species for most product groups with the same carbon number, not even the C_2 groups, under the present conditions, except C_{12} for which the 1-dodecene yield was substantially higher than dodecane for 6-30 min runs.

2. Reaction mechanisms of n - C_{14} pyrolysis. 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 under the high-pressure pyrolytic conditions. Scheme I shows the proposed reaction mechanisms in general form for thermal cracking of unbranched long-chain alkanes under the conditions employed [Song et al., 1992d]. There is no doubt that the pyrolysis of n -tetradecane proceeds by radical reaction pathways. As in every radical chain mechanism, the elementary reactions include initiation (eq. 1), propagation (eqs. 2-9), and termination (eq. 10). The propagation reactions can be divided into hydrogen abstraction (eqs. 2,3, 6,7), radical decomposition (eqs. 4, 5, 9), radical addition (which is the opposite of radical decomposition), and radical isomerization (eq. 8). To assist in the mechanistic discussion, Table 3 gives the Arrhenius parameters (activation energy, preexponential factor A , rate constant) for relevant elementary reactions of some small radicals (mostly C_1 - C_6) reported in the literature [Allara and Shaw, 1980; Domine et al., 1990; Schmich et al., 1992]. Recently Willems and Froment [1988a, 1988b] have reported the procedure for calculating the Arrhenius parameters for reactions of small radicals by means of a group contribution method based on the principles established by Benson [1976]. The Arrhenius parameters for larger radicals are not available, but the relative order of activation energies for different reactions of C_4 - C_6 radicals are considered to be applicable to larger radicals.

The initiation reaction is the homolytic cleavage of a carbon-carbon bond, producing two radicals (eq. 1). These radicals then abstract hydrogen from a molecule, mostly from the reactant substrate in the initial stage, and also from paraffinic and olefinic products in later stages. The first substrate (parent) radicals from n - C_{14} are mainly secondary radicals, sec - $C_{14}H_{29}^{\bullet}$ (eq.2), together with small amount ($< 10\%$) of primary radical pri - $C_{14}H_{29}^{\bullet}$ (in eq. 3). Formation of the primary radical by H-abstraction requires a higher activation energy, e.g., the activation energies required for H-abstraction by a radical from n -hexane to form 2- $C_6H_{13}^{\bullet}$ and 1- $C_6H_{13}^{\bullet}$ are 10.4 and 12.3 kcal/mol, respectively.

The substrate sec - $C_mH_{2m+1}^{\bullet}$ radicals undergo β -scission (eq. 4: cleavage of a C-C bond in the β -position with respect to the free electron) to form an alkene $1-C_nH_{2n}$ and a primary radical pri - $C_{m-n}H_{2(m-n)+1}^{\bullet}$ which then undergo one of the following three competing reactions that also apply to the primary radicals from the substrate, pri - $C_mH_{2m+1}^{\bullet}$ (eq. 3). The first is H-abstraction (eq. 6); the second is β -scission to produce ethylene and another pri -

$C_{m-n-2}H_{2(m-n-2)+1}\cdot$ radical; the third is isomerization from a primary radical to a secondary radical (eq. 8) which then undergoes β -scission (eq. 9) followed by the stabilization of the resulting primary radical by H-abstraction (eq. 6).

At low conversions of n-tetradecane (≤ 4 mol %), the carbon number distribution of the C_1 - C_{11} paraffinic and C_2 - C_{12} olefinic products is broad and there is not much selectivity (Table 2 and Figure 10). There are two reasons for the largely non-selective product distribution of the initial pyrolysis. First, the energy to abstract any secondary hydrogen from long-chain alkanes (eq. 2) such as n-tetradecane is about the same. 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 (eq. 1) with ≥ 2 carbon atoms. Supporting evidence for this consideration can be found from the known Arrhenius parameters for three different hydrogen abstraction reactions of n-hexane by an ethyl radical [Domine et al., 1990] and three different initiation reactions of n-hexane [Allara and Shaw, 1980], as shown in Table 3.

A question that arises then is why there is very little n-dodecane but 1-dodecene is dominant among the C_{12} products at low conversions? We believe this is because different reaction pathways are involved in the formation of these two compounds. As shown in Scheme II, in the initial reaction stage of C_mH_{2m+2} , a secondary $C_mH_{2m+1}\cdot$ radical of the substrate afford the m-2 olefinic product $C_{m-2}H_{2(m-2)}$ (1-dodecene from 1-tetradecene, eq. 4-I), whereas the m-2 paraffinic product $C_{m-2}H_{2(m-2)+2}$ (n-dodecane from n-tetradecane) can only be formed from β -scission of a primary $C_mH_{2m+1}\cdot$ radical followed by hydrogen abstraction (eqs. 5-I and 6-I). The very high 1-dodecene/n-dodecane ratio is due to two factors: 1) the very low population of the *pri*- $C_mH_{2m+1}\cdot$ radical, as mentioned above, and 2) the competition of the isomerization reaction of long-chain primary radical with its decomposition, as we further describe below.

It is well known at high-temperature ($\geq 550^\circ\text{C}$), low-pressure (atmospheric pressure), short-residence-time (< 1 min) conditions, as employed in most previous work related to industrial pyrolysis, radicals tend to undergo β -scission which leads to products rich in ethylene and 1-alkenes. Such pyrolysis reactions can be described by the well-known Rice-Kossiakoff mechanism [Rice, 1933; Kossiakoff and Rice, 1943]. Under our conditions, ethane is always more abundant than ethylene. Moreover, the ratios of 1-alkene to n-alkane for C_2 - C_{13} products are much lower than those for vapor-phase pyrolysis of long-chain alkanes reported in the literature, where most of the major products are 1-alkenes, and ethane and methane are the only significant paraffinic products [Zhou et al., 1987; Fairburn et al., 1990]. The pyrolysis under our conditions (about 2.4–8.9 MPa system pressure at 450°C) leads to more alkanes, which are closer to the conditions for applying the Fabuss-Smith-Satterfield

(one-step and two-step decomposition) mechanism [Fabuss et al., 1964]. Under high-pressure conditions, which in general tend to enhance bimolecular reactions, β -scission will be in competition with hydrogen abstraction.

The flat carbon number distribution of products (Figure 10) at low conversion (≤ 4 mol %), especially the almost equal molar distribution of C_2 - C_{12} 1-alkenes, suggests that the first radical formed by β -scission of $C_{14}H_{29}^\bullet$ radicals (eqs. 4,5) will already prefer to undergo hydrogen-abstraction (eq. 6), which yields one 1-alkene molecule and one alkane molecule, rather than a second-step β -scission to produce ethylene and another smaller radical, which would have led to ethylene-rich products. This is probably because the H-abstraction by a primary radical from a hydrocarbon is kinetically favored within the first 6 min (as we further describe below). For a given radical can undergo either β -scission or hydrogen abstraction; the activation energy required for a bimolecular H-abstraction is lower than that for a unimolecular β -scission. Supporting evidence can be found by comparing the Arrhenius parameters for H-abstraction and β -scission in Table 3: the activation energy for β -scission of $1-C_5H_{11}^\bullet$ to form $1-C_3H_7^\bullet$ plus C_2H_4 is 29 kcal/mol (reaction no. 50), while that for its H-abstraction from another paraffinic hydrocarbon is about 10 kcal/mol (no. 24). These mechanistic considerations rationalize the well-known experimental observations: low temperature and high pressure favor H-abstraction, but higher temperature and lower pressure facilitate β -scission.

When the n - C_{14} conversion increased to 17 mol % (Table 2, Figure 10) which corresponds to a 12 min residence time, there appeared a selectively enhanced formation of 1-hexene and 1-pentene from n - C_{14} (Figure 10). This kind of product distribution has not been reported in previous publications on pyrolysis of long-chain alkanes. We propose a facile isomerization of primary radicals to account for such selectivity. The preferential formation of 1-hexene may be attributed to a 1,5-shift coiling-type isomerization of a primary radical generated from substrate molecule, as shown in Scheme III. Similarly, the preferential formation of 1-pentene may be attributed to a 1,4-shift isomerization of a primary radical followed by the β -scission, as also shown in Scheme III. From the perspective of coiling or "curling up" of alkane chains, this type of isomerization should be easier for larger radicals than for smaller radicals. To enhance the selective formation of 1-hexene and 1-pentene, respectively, the chain length of primary radicals must be $\geq C_7$ for 1,5-shift and be $\geq C_6$ for 1,4-shift isomerization. As shown in Scheme III, the 1,5-shift and 1,4-shift also contribute to the increased formation of 1-propyl and ethyl radicals, respectively, which lead to the corresponding alkanes upon H-abstraction. Evidence for the primary-radical-initiated isomerization also comes from recent work on H-transferring pyrolysis, where we have found that adding hydrogen donors such as tetralin strongly suppressed the preferential formation of

1-pentene and 1-hexene, giving a flat distribution pattern of C₃-C₁₂ 1-alkenes [Song et al., 1993b]. This observation supports the above mechanistic consideration, because primary radicals tend to be scavenged preferentially by H-donation from tetralin; thus their isomerization reactions are suppressed significantly.

From the above discussion, the question as to why these isomerization reactions did not happen in the first 6 min arises naturally. This question may be answered with the aid of the temperature profile of the reactor. It is clear from Figure 7 that the first 6 min involves mainly heat-up of n-C₁₄, and its residence time between 420-450 °C was only 2 min within this period. Taking the kinetics of radical reactions into account, it is low-activation-energy reactions that are favored by lower temperature, in terms of relative rate. The intermolecular H-transfer reactions of a primary radical requires relatively lower energy of activation than its isomerization, which can be viewed as intramolecular H-transfer. Supporting evidence can be found by comparing the Arrhenius parameters in Table 3 for the H-transfer (reaction no. 24, 29, 40) and isomerization of 1-pentyl (no. 70), 1-hexyl (no. 72) and 1-heptyl radical (no. 74).

It should also be mentioned that we also detected small amounts of internal alkenes in addition to terminal alkenes. For example, both 1-hexene and 2-hexene were formed during n-C₁₄ pyrolysis at 450°C for 30 min in three repeated runs, but the yield of terminal alkene was always five times that of internal alkene. Therefore, it is clear that β -scission is the major pathway to olefinic products. In contrast to this pathway, the internal alkenes are probably formed by the so-called radical disproportionation reaction (Table 3), which refers to H-abstraction by a radical from a secondary radical. Another possible pathway to internal alkenes is the double bond isomerization, as reported by Shabtai et al. [1979] under the conditions of hydropyrolysis. Such reaction proceeds by abstraction of an allylic hydrogen from the terminal alkene, followed by double bond migration to form a primary but allyl-type radical followed by H-abstraction to produce an internal alkene.

With further increase in residence time or conversion, the peak of carbon number distribution for olefinic products shifts toward 3. After 1 h, the propylene yield becomes the highest among all the olefins (Figure 10) and this trend did not vary even after 480 min (Table 2). This is due in part to the fact that the 1-alkenes larger than C₄ can still undergo the H-abstraction followed by β -scission reaction, whereas propylene does not decompose to any significant extent under the conditions used. When it undergoes H-abstraction, it will form a allyl radical which is more stable than the other radical, and this radical does not undergo β -scission to any significant extent.

Further examination of Figure 4 at higher conversions (longer residence time) raises another question: why the yield of ethane is always higher than methane. The answer to this question also explains in part why there is very little C₁₃ products from n-C₁₄ pyrolysis.

Methane is produced from methyl radical upon hydrogen abstraction. Only certain radicals, upon β -scission, can generate methyl (from 3-R $\cdot$) or ethyl radicals (from 4-R $\cdot$). The β -scission of the radical 3-C_mH_{2m+1} $\cdot$ could produce two pairs of products: 1) an alkene 1-C_{m-1}H_(2m-1) plus CH₃ $\cdot$, and 2) 1-butene plus *pri*-C_{m-4}H_{(2m-4)+1} $\cdot$ radical. The latter will be formed preferentially when $m > 5$ because methyl radical is much less stable than any other alkyl radical. However, for the substrate radical 4-C_mH_{2m+1} $\cdot$, its β -scission could produce two pairs of products: 1) an alkene 1-C_{m-2}H_(2m-2) plus C₂H₅ $\cdot$, and 2) 1-pentene plus *pri*-C_{m-5}H_{(2m-5)+1} $\cdot$ radical; the probability for the two pairs is very similar. These considerations seem to be reasonable from the Arrhenius parameters reported by Allara and Shaw [1980]. For example, the former reaction of 3-C_mH_{2m+1} $\cdot$ in the case of a 3-octyl radical requires 33 kcal/mol, while the latter requires 29 kcal/mol (Table 3). On the other hand, both the activation energy and the A-factor values are similar for the formation of different pairs of 1-alkene and one radical with ≥ 2 carbon atoms from 4-C_mH_{2m+1} $\cdot$ radicals.

Table 2 indicates that higher alkanes such as pentadecane, hexadecane, heptadecane, and octadecane were also formed in small amounts from n-C₁₄ after 6–150 min at 450°C. These products have 1–9 more carbon atoms in their chain than the starting material n-C₁₄, indicating the occurrence of radical recombination between two radicals C_mH_{2m+1} $\cdot$ and C_nH_{2n+1} $\cdot$ (eq.10, Scheme I) and alkylation of the olefinic products by the radicals. These higher alkanes begin to diminish after 1 h at 450°C. Detailed GC-MS and GC analyses of liquid products in the present work indicate that the major C₁₅ to C₂₀ alkanes are normal straight-chain alkanes, and the branched higher alkanes are minor products, as shown in Figure 11. This suggests the major pathway for chain re-synthesis to be the combination of two primary radicals. The formation of C₁₅-C₂₃ branched alkanes, though in smaller amounts than the C₁₅-C₂₃ normal alkanes, is probably due to either the alkylation reactions or the combination of a primary and a secondary radical. In regard to the alkylation of the alkene, Ford [1986] reported that, during liquid-phase pyrolysis of n-hexadecane, the alkylation of the alkene by the radicals can produce C₁₈ to C₃₀ branched alkanes. The activation energies for the addition of radicals to olefins are fairly low, about 6–10 kcal/mol, as can be seen from Table 3. During the pyrolysis of a long-chain alkane C_mH_{2m+2} under the conditions employed, a major portion of the 1-alkene product with $m-1$ and m carbon atoms is probably formed indirectly from the decomposition of higher alkanes C_{m+n}H_{2(m+n)+2}.

There are some other interesting trends of the present results when compared to the data of Mushrush and Hazlett [1984], who reported the pyrolysis of n-hexadecane in a batch reactor. Although the same reaction temperature (450°C) was used in their work and the present work, they obtained liquid products where alkenes are more abundant than n-alkanes with the same carbon number even after 30 and 60 min run at 450 °C. For a 30 min stress,

alkenes were almost five times the alkanes. This is in distinct contrast to our data shown in Figures 9 and 10. This is mainly because the pressure in their pyrolysis experiments (several atmospheres) was much lower than that in the present work (Figure 8: more than 24 atmospheres). Higher pressure favors the bimolecular H-transfer, which leads to more alkanes, whereas lower pressure favors β -scission, that gives more olefins. Recently, we have found that for pyrolysis of a hydrocarbon at the same temperature using the same reactor, changes in the amounts of the sample initially charged and differences in the initial N_2 pressure for the same amount of a given sample can result in significant differences of the results, not only in rate and the extent of conversion, but also in product distribution. A detailed study is now in progress, and the results will be published in the near future.

3. Fate of long-chain olefinic products. Most previous pyrolysis work used very short residence times in a flow reactor, where maximum yields of alkenes are obtained. However, in long duration pyrolysis, the yields of alkenes vary considerably with residence time. Figure 12 shows the change of product yields as a function of residence time. A general trend observed from Figure 12 is that the yields of C_4 - C_{12} 1-alkenes reached maximum values in relatively short periods and then start to decrease, whereas the corresponding n-alkanes, including n-dodecane, further increased with increasing time up to certain residence time; then the yields of C_5 - C_{13} alkanes also decrease, as shown in Figure 12 and Table 2.

For the products in the C_8 - C_{13} range, both paraffinic and olefinic products decompose in the later stages, but alkenes diminish prior to the decline of alkanes. This is due to four kinds of reactions in the later stages: 1) decomposition; 2) the formation of diene from 1-alkene followed by cyclization and dehydrogenation; 3) hydrogenation of the alkenes by the hydrogen generated in situ; and 4) alkylation of alkenes by radicals. For the first reaction, Rebick [1979] has reported on the pyrolysis of α -olefins (1-alkenes). Higher selectivity towards the formation of $C_{m-3}H_{2m-6}$ was observed, and a concerted mechanism was proposed to account for this product. We will describe the second reaction in the following section. For alkene hydrogenation, the possible mechanism is shown in Scheme IV. GC analysis indicated the presence of molecular H_2 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 2. Apparently, H_2 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 H_2 . Shabtai et al. [1979] also proposed a similar mechanism for alkene hydrogenation during hydrolysis. Such radical H-abstraction reactions require relatively low activation energy, e.g., 15.2, and 16.0 kcal/mol for $C_2H_5^\bullet$ and $1-C_3H_7^\bullet$ respectively (lower than those for β -scission, see Table 3). When the free hydrogen becomes available, the alkene hydrogenation (eq. 9) 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-alkyl radicals are as low as 1.2–1.5 kcal/mol. It should be noted that if the hydrogen for abstraction reaction (eq. 12) is not readily available, the secondary radical generated from the addition reaction (eq. 11) can produce propylene selectively upon β -scission. Finally, the alkylation of alkenes by radicals can lead to alkanes upon H-abstraction by the resulting radicals. The relative contributions of the four reaction paths at different stages remain to be determined.

4. Formation of cyclic compounds. Little has been reported in previous publications on the formation of cyclic compounds during pyrolysis of long-chain alkanes. Many cyclic hydrocarbons were detected in our products, and this is apparently due to the long residence time. Figure 13 shows the distribution of cyclic compounds as a function of residence time. It is clear from Figure 13 and Table 2 that, in the liquid products, alkenes begin to decrease before cycloalkane formation becomes significant, cyclohexanes appear before alkylbenzenes, and 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]. No solid deposits were observed within the first 60 min. Measureable quantities of deposits (1–4.7 wt %) were formed on the reactor wall after 150–480 min. Within the first 30 min, the major cyclic products are cyclohexanes (0.7 mol %) and cyclopentanes (1.71 mol %). After 60 min, the formation of alkylbenzenes become significant. Cycloalkenes, mainly cyclohexenes, are considered to be the precursors to the alkylbenzenes.

Cyclic compounds can be formed from alkenes at least in two different pathways. The first is the well known Diels-Alder type reactions. Under the conditions used (450 °C), the formation of diene from alkene is not a very difficult reaction. The ease of abstraction of hydrogen atoms from various hydrocarbons decreases in the order of allylic > tertiary > secondary > primary > CH₄ > vinylic; hence the stability of free radicals increases in the order of vinyl < methyl < primary < secondary < tertiary < allyl. The activation energies for abstracting allylic hydrogens are considerably lower than for paraffinic hydrogens; the quantitative differences can be seen from Table 3 by comparing the Arrhenius parameters for reaction no. 15 and no.36. When the concentrations of alkenes reach certain level, they begin to participate in the hydrogen-transfer reactions, leading to the formation of a conjugated diene. Nohara and Sakai [1992] have recently demonstrated that cyclic alkenes can be formed from the Diels-Alder type reactions of butadiene with an alkene at ≥ 380 °C. Once a cyclohexene is formed, the subsequent dehydrogenation reaction can occur very rapidly because of the continued generation of radicals, which abstract hydrogen from the ring, leading to alkylbenzenes. As a result, more cyclic and, subsequently, aromatic hydrocarbons are formed in the long-duration pyrolysis. However, it should be kept in mind that the

aromatic compounds are not directly produced from $n\text{-C}_{14}$, but rather from the secondary reactions of its primary pyrolysis products.

Another type of cyclization reaction is the ring closure of an olefinic radical, for example, 5-hexenyl radical. Probably this type of reaction is responsible for the formation of certain cyclic compounds, at least methylcyclopentane. The intramolecular hydrogen transfer of 5-hexenyl radical results in closure to mainly the five-membered ring, together with small amount of six-membered ring product, as shown in Scheme V. This is opposite to what one would expect from the viewpoint of radical stability, but this stability factor is less important than the steric factor in the ring-closure reaction. Supporting evidence can be found in the literature. Lamb et al. [1963] observed the preferential formation of methylcyclopentane, together with a very small amount of cyclohexane, during thermal decomposition of 6-heptenoyl peroxide. This is due to the cyclization of the intermediate 5-hexenyl radical, followed by hydrogen abstraction. Lal et al. [1974] have reported the rate constant for the cyclization of the 5-hexenyl radical to the cyclopentylmethyl radical (10^5 s^{-1} at 25°C). For the ring-closure reactions in synthetic organic chemistry, the favored pathways are those which enable the terminal atoms to achieve the proper geometries for reaction [Baldwin et al., 1976, 1982; March, 1985].

Cyclopentanes can also be formed from the isomerization of cyclohexanes. In a recent study on pyrolysis of cycloalkanes, we have observed the isomerization of ethylcyclohexane into C_3 -cyclopentanes under comparable conditions [Song et al., 1992c].

Summary

The present work provided some fundamental information on the characteristic distribution of products from pyrolysis of n -tetradecane at 450°C under elevated pressures for long duration, the shift of carbon number distribution for both paraffinic and olefinic products with increase in residence time, and the mechanisms for radical reactions. Such information is important in considering the pyrolytic degradation of long-chain alkanes during high-temperature thermal stressing of jet fuels to be encountered in high-Mach flight of advanced jet aircraft.

For pyrolysis of a long-chain alkane $\text{C}_m\text{H}_{2m+2}$ ($m=14$ for n -tetradecane) at 450°C under elevated pressures (about 2-9 MPa) for 6-480 min, the major products in the initial stage are n -alkanes in the carbon number range of C_1 - to C_{m-3} and terminal 1-alkenes in the carbon number range of C_2 - to C_{m-2} . Among the paraffinic products within first 12 min, there are very few compounds with $m-2$ and $m-1$ carbon atoms. Among the olefinic products, formation of the compound with $m-1$ carbon atoms is very limited in the initial stage. As compared to the well-known gas-phase pyrolysis, the molar ratios of alkenes to

alkanes are much smaller (around 1 and below), except the ratio for the group with $m-2$ carbon atoms, where the ratio of 1-alkene to n -alkane can be as high as 9 in the initial stage. This is because terminal alkene $1-C_{m-2}H_{2(m-2)}$ is produced from β -scission of secondary radical $4-C_mH_{2m+1}\bullet$, whereas $n-C_{m-2}H_{2(m-2)+2}$ is formed from a primary radical $1-C_mH_{2m+1}\bullet$, whose population is much less than the secondary radical due to both higher activation energy and the competing isomerization reaction.

There appeared a preferential formation of 1-hexene and 1-pentene among the 1-alkenes formed after 12 min. This may be attributed to the 1,5-shift and 1,4-shift isomerization of primary radicals formed during tetradecane pyrolysis. The peak of carbon number distribution shifts towards 2 for paraffinic products and towards 3 for olefinic products, and the ratios of alkenes to alkanes decrease with increasing residence time up to 150 min.

The substrate alkane molecules are the source for hydrogen abstraction in the initial periods, but in the later stages the olefinic products also undergo the H-abstraction reactions, which lead to the formation of cyclic compounds such as cyclohexanes, cyclopentanes and alkylaromatics which include mainly alkylbenzenes, together with smaller amounts of alkyl-substituted indanes and naphthalenes. The possible pathways leading to cyclic alkanes and alkenes include Diels-Alder type reactions and intramolecular addition of olefinic radicals leading to ring closure. Considerable deposit formation was observed when aromatics formation became significant after long residence time (150 min) at 450 °C.

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3. Surface Effects on the Formation of Carbon Deposits from Thermal Stressing of JetA Fuel and n-Dodecane (Contributed by Jun Li and Semih Eser)

Introduction

Previous studies showed that the chemical composition of a metal surface (in the form of transmission electron microscope (TEM) grids) as well as the starting materials had a significant effect on carbon deposit formation during thermal stressing of Jet A and n-

dodecane [1]. Basically, three different growth patterns of carbonaceous deposit were found in n-dodecane: lateral growth on nickel and titanium grids; perpendicular growth on stainless steel and gold grids; and lateral and perpendicular growth on copper grids. Jet A was seen to be more reactive than n-dodecane in generating carbon deposits under the same conditions.

In this quarter, TEM grids were placed at the top and the bottom of the reactors before thermal stressing with Jet A and n-dodecane, to study the deposition processes at the top and bottom of the reactors. One of the motivations for this study is to get information on the existing phases during thermal stressing within a microautoclave, based on the observed microstructures of the carbonaceous solid. Optical textures and morphologies of carbonaceous deposits generated on reactor walls and on metal grid surfaces from Jet A and n-dodecane at 450 °C for 1, 3, and 5 hours were examined using polarized-light optical microscopy (PLM) and scanning electron microscopy (SEM). The metal grid-deposit interface was also examined by PLM. In addition, the effect of surface roughness on deposit formation was also studied, since the grids inherently contain smooth and rough surfaces.

Experimental

Thermal stressing of Jet A (Shell) and n-dodecane (Aldrich Chemical, >99%) were conducted isothermally in 20 mL stainless steel (316) tubing bomb reactors heated in a fluidized sand bath. A 5 mL sample was used for all the tests. The sample was deoxygenated by repetitive pressurization and purging (at least 5 times) with ultra-high purity (UHP) nitrogen, and left with 0.69 MPa (100 psi) UHD N₂ as the initial pressure. At the end of the reaction, the reactor was quenched in cold water. Solid deposits from top and bottom reactor walls were collected separately.

Ni, Cu, and stainless steel (SS) grids (Polysciences, Inc.) were placed at the bottom of the reactors and hung at the top of the reactor by a fine copper wire. Both Ni and Cu grids had a polished, smooth side and a dull, rough side. The SS grids had no specific finishing, but were cut in a way to introduce rough edges.

SEM examination was conducted using an ISI ABT SX-40A microscope. A Nikon Microphot FXA-II. polarized-light microscope (PLM) was used to study the optical textures of the deposits. The grids were embedded in epoxy resin in such a way that, after polishing, the cross section of the grids, deposits and the grid-deposit interface can be examined.

Results and Discussion

1. Carbon Deposition From Jet A. All the carbonaceous deposits produced on grid surfaces or on reactor walls are optically anisotropic, but they displayed substantial microstructural differences, depending on the metal grid used and its position in the reactor.

Ni grids become very brittle after 1 hour of reaction with jet fuel, and they usually rupture after 5 hours reaction. This behavior is not observed for Cu or SS grids or Ni grids reacted with dodecane. Ni grids become very brittle after 1 hour reaction and their original structure is usually ruptured after 5 hour reaction. This is not seen for Cu and SS grids or Ni grids in dodecane.

Carbonaceous solids collected from both the top and bottom of the reactor wall contained flaky deposits with typical pyrolytic carbon microstructures resulting from gas-phase reaction, as shown by PLM in Figure 14a [2]. Some deposits obtained from the bottom of the reactors showed signs of liquid-phase reactions resembling the formation of carbonaceous mesophase, as shown in Figure 14b [2].

Figure 15 shows the interface of a Ni grid and the carbonaceous deposit collected after thermal stressing of Jet A at 450 °C for 3 hours. It can be seen from Figures 15a and 15b that some Ni particles were lifted from the surface of the grid and encapsulated in the carbon deposit after a 3 hour test. Carbonaceous deposit was accumulated on both smooth and rough sides of the Ni grid. The PLM micrographs of the interface of Cu grid with the deposits also showed that deposit was collected in equal amounts on both the smooth and rough sides of the Cu grids. For SS grids, carbon deposit was collected on both sides without any preference between the smooth surfaces and the rough edges when the grids were placed at the bottom of the reactors.

Figure 16a shows the SEM micrographs, indicating a thin layer of discrete crystallites on the rough surface of the Ni grid placed at the top of a reactor and stressed for 1 hour. The highly crystalline morphology of the deposit particles shown in Figure 16a is rather unusual, suggesting the formation of nickel carbide or another solid crystal. A more amorphous and much thinner layer of deposits were seen on an SS grid (Figure 16b) stressed under the same conditions as the Ni grid. This observation shows the much higher activity of a nickel surface than a stainless steel surface for incipient deposition. Top grids usually have more extensive deposition than those placed at the bottom. The microstructures of the carbon deposits formed on top grids are somewhat different from those placed at the bottom of the reactors. Usually, the deposit on top grids has a finer particulate structure, while deposits on the bottom grids deposits appear to be more bulky with discrete spherules of carbonaceous matter on the uppermost layer. Figure 17 shows carbon deposition after 3 hours on grids placed at bottom of the reactors; Ni (Figure 17a), Cu (Figure 17b), and SS grids (Figure 17c). Three distinct forms of carbon deposit can be seen: a continuous bulky layer at the bottom covering the entire grid; coalesced spherules on the bulky layer; and dispersed small spherules at the very top of the deposits. These structures, along with the optical microscopic observations, suggest that the process of deposition on the grids starts by a vapor-phase

nucleation of spherulites which diffuse onto grid surfaces, most probably as liquid-like droplets, and coalesce and carbonize further on the surface to form continuous deposit layers.

2. Carbon Deposition From n-Dodecane. The solid deposits recovered from the top and the bottom of the reactors showed similar microstructures to those obtained from stressing Jet A fuel. The deposits obtained from the top of the reactor showed, more distinctly, a sequential growth pattern in which liquid-like spherulites nucleated in the vapor phase become incorporated into a surface layer by further compaction and carbonization in a fluid phase, as shown in Figure 18a. Figure 18b shows the coarser structures of the bottom wall deposits formed by preferential growth on selected regions of incipient deposits.

There were more readily observable differences between the behavior of different grids during n-dodecane stressing. In general, the deposits obtained from n-dodecane appeared to be more homogeneous in micro structure than those produced from Jet A. This difference is presumably due to a more varied composition of deposit precursors generated during Jet A stressing. The SEM examination of the grids showed, as observed before [1], different growth patterns on each grid. Ni grids showed a lateral growth of deposits on the surface, suggesting a strong surface diffusion of deposit precursors and a possible catalytic effect. In contrast, SS grids show deposit growth perpendicular to the grid surface on incipient deposits, indicating the surface of nascent deposits is more attractive for further growth than bare metal surface. Cu grids, on the other hand, showed both lateral and perpendicular growth patterns, suggesting some catalytic effect.

The surface roughness of the grids appeared to have different effects, or no effect at all, depending on the metal composition and the position in the reactor. There were more deposits, for example, on the rough side of the Ni grids reacted with dodecane, but no preference when reacted with the Jet A fuel. The Cu grids showed no effects of the surface roughness when reacted with n-dodecane or Jet A fuel. The SS grids, on the other hand, showed no preference between the smooth and rough surfaces when the grid was placed at the bottom of the reactor, Figure 19b. At the top of the reactor, however, there were more deposits on the rough edges than on smooth surfaces of the SS grid, Figure 19a. This difference in preferential deposition, combined with more extensive deposition at the top of the reactor, suggests a surface-sensitive deposition at the top of the reactors, whereas fluid-phase nucleation and diffusion of spherules onto the metal surfaces appear to control the deposition process at the bottom of the reactors. Although there is not much evidence for a phase separation between the top and the bottom of the reactors, there appears to be a difference between the chemical composition of the deposit precursors at the top and bottom of the reactors.

Conclusions

The microscopic examination of carbonaceous deposits collected on different metal grids indicates a layer-by-layer growth of solid deposits on surfaces primarily by incorporation of liquid-like spherules nucleated in a vapor phase and diffused onto the substrates. Ni grids appear to have a strong catalytic effect on incipient deposit formation from Jet A fuel. Ni, among other group VIII metals, has been well identified as a catalyst for carbon formation [3]. Cu grids also showed some catalysis of incipient deposition, whereas stainless steel grids did not show any catalytic effect. The deposits produced from Jet A appear to be more heterogeneous in structure than those from n-dodecane, presumably due to a greater variety of deposit precursors generated during Jet A reactions.

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Task 2. Investigation of Incipient Deposition

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

Introduction

Evidence from our previous work with coal-derived jet fuel (JP-8C) suggested that solid deposits were formed on the vertical surfaces of the static tubing bomb reactor by direct addition of reactive species to the wall from the fluid, but that deposits on the bottom of the reactor formed by gravitational settling of particles formed in suspension. The experiment was modified to enable us to make a quantitative comparison of settling and deposition rates.

Measurements

Mixtures of JP-8C and tetradecane covering the entire range of compositions were stressed for 6 hours at 450°C under nitrogen. Instead of lumping all of the solid material together, the following components were collected and weighed separately:

1. Deposit on the bottom of the reactor.
2. Deposit on the side walls of the reactor.
3. Deposit inside the top of the reactor.
4. Suspended particles, separated from the liquid by filtration.

The total mass of solid material as a fraction of the mass charged to the reactor is shown in Figure 20a. The concentration of particles, obtained by dividing the mass of particles by the volume of the reactor, is shown in Figure 20b. The deposits on the sides and bottom, per unit of projected area, are shown in Figures 20c and 20d, respectively. Particle size distributions were determined for some samples using a Malvern Droplet and Particle Sizer, after several days. A typical volume-based size distribution contained peaks at 3 and 10 μm .

Discussion

The product of particle concentration and settling velocity was equated to the average rate of deposit growth per unit area on the bottom of the reactor. The settling velocity was obtained from Stokes' law, assuming that fuel vapor completely and uniformly filled the enclosure. The resulting relation was solved for the size of particles which would settle at the observed deposition rate. Particle density was assumed to be 1200 kg/m^3 . The calculated sizes, in the cases thought to have reached approximately steady state in 6 hours (tetradecane >20 wt%), varied only from 1.7 to 2.1 μm , not far from the 3 μm peak observed in the size distributions. Manipulation of the equations shows that the size of the settling particles is insensitive to the particle formation and deposition rates. Settling is therefore a plausible mechanism for the growth of deposit on the bottom of the reactor. Refinements of this analysis will attempt to account for the presence of larger particles ($\approx 10 \mu\text{m}$) in the samples, and a measurement of the density of the particles is needed to better estimate their settling velocity.

The next step in this study is to determine if the formation and deposition reactions of a single class of reactive species can explain the observed rate of deposit growth on the vertical walls and the rate of formation of the suspended particles.

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

Effects of Adding Solid Carbons on Thermal Degradation of Jet Fuel (Contributed by Katia Gergova, Rathnamala Arumugam, and Semih Eser)

Introduction

Different solid carbons were added to JP-8 jet fuel to investigate the effects of carbon surfaces on solid deposition and on the chemistry of thermal degradation. We conducted thermal stressing of JP-8 jet fuel in the presence of two different activated carbons, carbon black, graphite spectroscopic powder SP-1, alumina and previously recovered carbonaceous deposits. Thermal stressing experiments were carried out at 450°C for 5 hours. A clear difference in the appearance of the liquid products was observed only with the addition of 1 g activated carbon to 10 ml of JP-8. The liquid obtained from the jet fuel heated with activated carbon was much lighter in color than the liquid from JP-8 stressed alone. The presence of all the added solid carbons appears to have a substantial influence on the deposition processes. Some of the added carbons (activated carbons, carbon black and graphite) prevent solid deposition during thermal stressing of JP-8 at 450°C for 5 hours, while the other solids (alumina and the deposit previously obtained from stressing of jet fuel) 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.

Different microstructures of the deposits observed on the added solid carbons indicate that the deposition mechanisms are also affected by the presence of different carbon surfaces during thermal stressing of the fuel. Evidently, the solid carbons with the most disordered structure and highest surface reactivity (i.e. activated carbons) produced the most significant effect on thermal degradation. The activated carbon surfaces appear to be effective in stabilizing the free radicals or catalyzing the recombination reactions to form more gases and to preserve constituent paraffins in the fuel at 450°C. However, it was not clear whether the surface area or the pore size distribution of the activated carbons is responsible for preventing the solid deposition and stabilizing the jet fuel during thermal stressing at 450°C. Also, the effects of activated carbon addition on the other jet fuel samples need to be investigated.

The main objective of this study is to investigate the effects of the surface area and pore size distribution of activated carbons on solid deposition as well as the thermal behavior of commercial jet fuels A-1 and JPTS in the presence of different solid carbons.

We also made an attempt to decrease substantially the amount of activated carbon added to jet fuels before thermal stressing at 450°C for 5 hours.

Experimental

Thermal stressing experiments were carried out on 10 mL samples of a JP-8 jet fuel mixed with 1 g samples of activated carbons from cherry stones, grape seeds, almond shells and anthracite. The experiments were conducted at 450°C for 5 hours. In addition, thermal stressing experiments were carried out on 10 mL JPTS jet fuels samples mixed with 1 g and 200 mg activated carbon from apricot shells with particle size 1–3 mm, powdered activated carbon, as well as a commercial activated carbon sample (Calgon) under the same heating conditions. Ten mL JPTS and A-1 jet fuel were also stressed with 100 and 200 mg of high surface area activated carbon PX-21. PX-21 carbon was produced by Amoco Oil Company and has a BET N₂ surface area of 3000 m²/g.

A Perkin-Elmer 8500 Gas Chromatograph with a fused silica capillary column was used for a quantitative analysis of the liquid products based on calibration curves obtained from external standards. In addition, the liquid products were analyzed by GC/MS using a Hewlett-Packard 5890 interfaced with a HP 5971A mass selective detector.

The activated carbons used were characterized by N₂ adsorption at 77 K using a Quantachrome automated adsorption apparatus, Autosorb-1, model ASIT. From the adsorption data, the BET surface areas and the pore size distributions were calculated using the procedure developed by Barrett, Joyner and Halenda [2]. The activated carbons before and after stressing with jet fuel samples as well as the carbonaceous deposits (if formed) were examined using a polarized-light microscope, Nikon-Microphot FXA.

Results and Discussion

1. Thermal Stressing of JP-8 Mixed with Different Activated Carbons.

Adsorption properties of the activated carbons: Table 4 shows the BET N₂ surface area and pore size distribution of the activated carbons used as additives in this study. The data in Table 4 indicate a wide variation of BET N₂ surface areas and pore size distributions among the activated carbons. It is well known that the high surface area of activated carbons is due mainly to their micropore volumes. The commercial activated carbon (Calgon) and the activated carbons from apricot stones and anthracite have high BET surface areas and micropore volumes. Activated carbons from cherry stones and grape seeds have a predominantly macro- and mesoporous structures, while the carbon from almond shells contains mainly mesoporous and microporous structure.

We conducted earlier thermal stressing of JP-8 jet fuel in the presence of 1 g activated carbon from apricot stones and the commercial activated carbon [1]. The effects of adding activated carbon were the prevention of solid deposition and preservation of the compounds present in the initial fuel sample. It was not quite clear, however, whether the activated carbon surface was effective in stabilizing the free radicals or the specific pore size distribution of the activated carbons was responsible for the stabilizing effect. If the pore size distribution were important in stabilizing the solid precursors, then meso- and macroporous activated carbons should be more effective than microporous carbons because the larger pores of meso- and macroporous carbons would allow the diffusion of larger molecules into their porous structures.

Yield of liquid and solid products: Ten mL of JP-8 jet fuel was mixed with samples of 1 g activated carbon produced from cherry stones, grape seeds, almond shells and anthracite and stressed at 450°C for 5 hours in vertical stainless steel microautoclaves. Table 5 summarizes the results obtained from these experiments. The liquids obtained from stressing of JP-8 with different activated carbons appeared to have a dark color similar to that of the liquid obtained from thermal stressing of JP-8 alone. The liquid obtained after stressing of JP-8 mixed with activated anthracite had a lighter color. It should be noted that the addition of all carbons, and especially activated carbon from anthracite, prevents the deposition of solid on the reactor walls. All the solid carbons gained weight during thermal stressing with JP-8 jet fuel at 450°C. Based on the microscopic study of the activated carbons after stressing with JP-8 jet fuel, we believe that part of the weight gained by the activated carbons is due to solid carbon deposit on the carbon surfaces (especially on the surface of activated carbons from grape seeds, cherry stones and almond shells). Activated anthracite gained much less weight than the other activated carbons. Considering that activated anthracite has a higher BET N₂ surface area (Table 4) than the other activated carbons used in these experiments, one can assume that activated anthracite adsorbs more liquid during thermal stressing (the liquid yield of JP-8 mixed with activated anthracite is 3.5 mL while the liquid yields of the JP-8 mixed with activated carbons from almond shells, cherry stones and grape seeds are 3.9, 4.0 and 4.2 mL, respectively). It should be noted that the activated carbons from grape seeds and cherry stones with lower BET surface area and predominantly meso- and macroporous structure created higher gas pressures in the reactor than activated carbons from almond shells and especially anthracite which have higher BET surface areas and predominantly microporous structure. The differences in the gas yields show that the addition of activated carbons with meso- and macroporous structure during thermal

stressing of jet fuel samples at 450°C promotes the cracking processes and increases the possibility of solid deposition on the reactor walls.

Microscopic examination of added carbons after stressing with JP-8 fuel samples at 450°C: Figures 21–24 show polarized-light micrographs of the activated carbons after stressing with JP-8 at 450°C for 5 hours. The activated carbons from grape seeds show almost an epitaxial growth of anisotropic carbonaceous deposit on outer surfaces of the carbons, as shown in Figure 21. Compared to the grape seed carbons, the activated carbons from cherry stones and almond shells have more closed structures with irregular distribution of pores as shown in Figure 22 and 23, respectively, but show similar deposition of carbonaceous solids on their outer surfaces. Apparently, all three activated carbons provide more attractive surfaces for carbon deposition than stainless steel reactor surfaces. In contrast, microporous carbons (e.g., apricot stone carbons and commercial activated carbon) used as additives previously did not show any significant solid deposition on their surfaces [1]. The deposit structures shown on the activated carbon surfaces in Figures 21–23 suggest liquid-phase carbonization reactions on the surface of the activated carbons of the deposit precursors which are mostly initiated in a vapor phase. There is a broad sheath of laminar pyrolytic carbon followed by a small band of isotropic material (Figure 21, activated carbon from grape seeds). The solid in Figure 23 shows pyrolytic carbon attached to an activated carbon surface which indicates cracks and fissures.

The carbonaceous deposits recovered with activated anthracite particles after thermal stressing with JP-8 (Figure 24) have different microstructures from those seen with the other activated carbons. These deposits are in the form of thin flakes showing, on one side, straight edges of pyrolytic carbon structures formed by gas-phase deposition reactions and, on the other, deposition of liquid-like spherulites nucleated probably in the vapor phase. Compared to the pyrolytic deposits obtained from the JP-8 stressed alone, the flaky solids mixed with activated anthracites are much thinner and evidently very loosely attached to the reactor walls. Similar to the behavior of other microporous carbons, the presence of activated anthracites suppressed the formation of carbonaceous deposits without any apparent deposition on the added carbon surfaces.

2. Thermal stressing of JPTS jet fuel with activated carbons. It appears that the activity of carbons in suppressing the deposit formation depends on their surface area. To investigate the behavior of other jet fuel samples with high-surface-area carbons, we stressed 10 mL samples of JPTS and Jet A-1 jet fuel mixed with 1 g commercial activated carbon (Calgon), activated carbon from apricot stones with particle size 1–3 mm, as well as powdered activated carbon from apricot stones. The results obtained are very similar

to the data obtained for JP-8 jet fuel stressed with the same activated carbons. Activated carbon from apricot stones-1-3 mm and commercial activated carbon Calgon inhibited the solid deposition and slowed down the degradation of jet fuel, while the powdered activated carbon from apricot stones did not have the same effect. It is not clear why the small particle activated carbon is not as effective as the large particles in suppressing the deposit formation.

Microscopic examination of deposit and activated carbons from thermal stressing of JPTS and A-1 jet fuels: Figure 25 shows the micrographs of activated carbons from apricot stones 1-3 mm (Position A) and commercial activated carbon Calgon (Position B) after thermal stressing with JPTS at 450°C for 5 hours. One can clearly see that both activated carbons have isotropic structures and no carbonaceous solid is deposited on the activated carbons' surfaces. In contrast, the micrographs of powdered activated carbon (Figure 26) show large quantities of carbonaceous solid deposited on the activated carbon surfaces. The structure of the solid deposits is different from those obtained after thermal stressing of JPTS and A-1 jet fuel alone under the same conditions, which were dominated by straight flakes of pyrolytic carbon microstructures, as shown in Figures 27 and 28, respectively.

3. Thermal stressing of jet fuel samples with 100 and 200 mg of a high surface area activated carbons. In efforts to reduce the amount of added activated carbons, we conducted thermal stressing of 10 mL JPTS jet fuel with 200 mg activated carbon from apricot stones as well as carbon from Calgon. The results obtained show that 200 mg activated carbon with BET surface area of approximately 1000 m²/g is not sufficient to prevent the formation of carbonaceous solids during thermal stressing of jet fuel at 450°C. A higher surface area activated carbon, PX-21, was used in additional experiments.

Figures 29 and 30 show the differences in the appearance of the liquids obtained after thermal stressing at 450°C of JPTS jet fuel mixed with 100 mg activated carbon PX-21 and A-1 jet fuel mixed with 200 mg activated carbon PX-21 compared to the liquid obtained after thermal stressing of JPTS and A-1 alone. It should be noted that the liquid obtained after thermal stressing of JPTS with 100 mg PX-21 is much lighter in color than the liquid obtained after thermal stressing of A-1 mixed with 200 mg PX-21. It should also be noted that a significant quantity of carbonaceous solids were produced from JPTS mixed with, but not on the surface of, the added carbons. Jet A-1, on the other hand, which gave a darker colored liquid product than JPTS, did not produce any apparent solids.

Table 6 shows the yield and composition of liquids obtained after thermal stressing of A-1 jet fuel alone and mixed with 200 mg high surface area activated carbon PX-21. The data in Table 6 indicate that both liquids are very complicated mixtures and they consist of similar compounds. An important difference in the composition of the liquids is that some of the C₅ and C₆ benzenes as well as two-, three- and even four-ring aromatic compounds such as: C₃ and C₄ naphthalenes, fluorenes, methylfluorenes, phenanthrenes, methylphenanthrenes, anthracene, pyrene and methylpyrene are present in the liquid obtained after thermal stressing of A-1 alone, but they are not present in the liquid obtained after thermal stressing of A-1 mixed with 200 mg PX-21 activated carbon. Most probably the darker color of the A-1 stressed without PX-21 is due to the increased concentration of polynuclear and alkyl-substituted polynuclear aromatic hydrocarbons. The polyaromatics and especially the alkylated polyaromatics, probably more complex in structure than those identified in the liquid product obtained after thermal stressing of A-1 at 450°C, are most likely the precursors to solid deposits.

As reported before for JP-8 jet fuel stressed with and without activated carbon, the concentration of short-chain alkanes (C₅-C₈) is higher in the sample obtained from thermal stressing of A-1 alone (Table 6). Most probably short-chain alkanes result from cracking processes during thermal stressing. It should be noted that cycloalkanes and alkyl-substituted cycloalkanes appear to be present in higher concentrations in stressed A-1 than in stressed JP-8 jet fuel. Their concentration in the liquid obtained after stressing of A-1 alone is higher than in the liquid obtained from the thermal stressing of A-1 with PX-21 activated carbon. Table 6 shows a comparison of weight percent for the long-chain alkanes (C₉-C₁₄) indicating that the concentration of long-chain paraffins, especially (C₁₀-C₁₂), is considerably higher for the liquid obtained from thermal stressing of A-1 mixed with activated carbon.

The data for the liquids obtained from stressing of A-1 alone and with activated carbon PX-21 show the same trends as the results previously reported for the JP-8 jet fuel stressed with and without activated carbon at the same heating conditions, but the amount of activated carbon added to A-1 jet fuel is 20% of the amount added to JP-8 jet fuel.

Figures 31-33 show a series of plots which were prepared to compare the relative concentrations of selected compounds in the liquids obtained after stressing of A-1 alone and with activated carbon PX-21.

Figure 31 shows the alkane carbon number as a function of weight percent for the liquids obtained after stressing of A-1 alone and with PX-21. n-Tridecane is not shown in the Figure 31 because it coelutes with C₅ benzenes. As shown in Figure 31, the liquid obtained from thermal stressing of A-1 without activated carbon has a higher

concentration of C₈ and almost the same concentration of C₉ alkanes. Further, a comparison of C₁₀, C₁₁ and C₁₂ weight percents obtained by GC indicates that these alkanes are in considerably higher concentrations in the liquid obtained from A-1 stressed with PX-21. It should be noted that tetradecane is not present in the liquid obtained from thermal stressing of A-1 but it appears in low concentration in the liquid obtained from stressing of A-1 mixed with PX-21.

In Figure 32 the number of alkyl groups on benzenes are plotted against weight percent for the A-1 stressed alone and with activated carbon PX-21. The sample obtained from the A-1 jet fuel stressed without carbon has a higher concentration of alkylbenzenes, especially toluene and benzene with two and three methyl groups. With the increasing number of methyl groups on benzene the concentration of alkylbenzenes in the liquid obtained from stressing of A-1 alone decreases. As can be seen from Figure 32, the concentration of C₄ and C₅ alkylbenzenes is higher for the samples obtained from stressing of A-1 with PX-21.

The number of alkyl-substituted naphthalene for the liquid samples obtained after thermal stressing of A-1 with and without carbon are plotted against the weight percent obtained by GC in Figure 33. The plot in Figure 33 clearly shows that the concentration of alkyl-substituted naphthalenes, and especially naphthalene, is higher for the liquid obtained after thermal stressing of A-1 jet fuel alone.

In the Figures 34-38 the percent weight of different compound groups such as alkane, alkene, cycloalkane, alkylbenzene and naphthalene for the liquids obtained after thermal stressing of A-1 jet fuel alone is plotted versus percent weight of the same compound groups, but for the liquid obtained after thermal stressing of A-1 mixed with 200 mg activated carbon PX-21. Figure 34 shows very clearly that the concentration of long-chain paraffins (C₉-C₁₄) is higher in the liquid obtained from stressing of A-1 with activated carbon. In Figure 35 one can see the same trends for alkenes. While the nonene and decene are predominantly in higher concentration in the liquid obtained from A-1 stressed with activated carbon, pentane and hexane are in higher concentration in the liquid obtained from the A-1 stressed alone. There is not a clear predominance of cycloalkanes in either one of the samples (Figure 36). However, Figures 37 and 38 show that, evidently, the liquid obtained from stressing of neat A-1 consists of higher concentrations of alkyl benzenes and naphthalenes.

Microscopic examination of activated carbon PX-21 after thermal stressing with jet fuel samples: The thermal stressing experiments were conducted with A-1 jet fuel mixed with 200 mg PX-21 activated carbon at 450°C, for 5 hours. Figure 39 shows the polarized-light micrographs of PX-21 activated carbon after thermal stressing with A-1

jet fuel. Polished surfaces of the activated carbon show reflectance interference colors characteristic of anisotropic carbons. One can clearly see that no carbonaceous solid is deposited on the activated carbon surface. Figure 40 shows that 100 mg activated carbon PX-21 stressed with JPTS jet fuel produced a considerable amount carbonaceous solids which are not deposited directly on the activated carbon surfaces. It appears that 100 mg PX-21 is not sufficient to suppress solid formation, despite the generation of a clear liquid product.

Conclusions

It appears that the specific surface area of the activated carbons used as additives is an important parameter which determines their effectiveness in suppressing solid deposition. Activated carbons with high specific surface areas and microporous structures appear to be the most effective carbon additives for inhibiting solid formation. The differences seen in the liquid product composition when solid carbons are added indicates a catalytic effect of the carbon surfaces during thermal degradation of jet fuels. Higher concentrations of paraffins and lower concentrations of alkylated aromatics are associated with the liquid products obtained in the presence of activated carbons.

References

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Task 4. Coal-based Fuel Stabilization Studies

1. Thermal Stability Studies Using the Model Compound Dodecane (Contributed by Leena Selvaraj, Maria Sobkowiak and Michael M. Coleman).

Introduction

The typical jet fuel is a highly complex mixture, which makes the analysis of the products of thermal degradation in the presence of additives very complicated. Having successfully performed scouting studies to find additives that retard the thermal degradation of the jet fuel at 425°C, we decided to simplify the experimental methodology in order to attempt to elucidate the underlying mechanisms involved. Understanding the reasons why benzyl alcohol and similar molecules retard the formation of carbonaceous solids in hydrocarbon mixtures at high temperatures is important and should point the way to the

design of superior additives in the future. Dodecane was chosen as the model compound as it is the most abundant hydrocarbon in jet fuels and there have been numerous studies performed on dodecane as a model.

Experimental

Two sets of experiments were initially performed, the first on pure dodecane and the second on dodecane with 5% benzyl alcohol by volume each stressed as a function of time. Thermal stressing was performed on 10 mL samples at 425°C in 15 mL type 316 stainless steel microreactors under 100 psi of air or nitrogen. The microreactor containing the sample was purged with UHP-grade N₂ five times at 1000 psi to minimize the presence of dissolved oxygen and finally pressurized with 100 psi of air. It was then placed in a preheated sand bath at 425°C for the required reaction time, followed by quenching into cold water and depressurizing to remove head-space gases.

Infrared spectra were obtained on a Digilab FTS-60 FTIR spectrometer using a sealed KBr liquid cell with a path length of 0.015 mm. A minimum of 64 coadded scans at a resolution of 2 cm⁻¹ were obtained. Samples for NMR analysis (50:50 w/w) were prepared in deuterated chloroform (99.96%). Spectra were recorded on a Bruker WP200 instrument at a field strength of 200 MHz.

Gas chromatographic studies were performed using a Hewlett Packard GC with a FID detector. The column used was Rtx-50. The temperature program used is as follows: initial temperature: 40°C, initial isotime: 5min, heating rate of 4°C/min to 280°C, and the final isotime 10min. The split mode of injection was used. The head-space gases were analysed using Perkin Elmer Autosystem GC with dual detectors (FID and TCD). A Hewlett Packard GC with mass detector was used for the analysis.

Discussion

1. Infrared Studies. Figure 41 shows the room temperature infrared spectra in the region 1550–1850 cm⁻¹ of samples thermally stressed under air after time periods of 0, 1, 3, 6, 12, and 18 h at 425°C. Note particularly the growth of the prominent band at approximately 1642 cm⁻¹ in the spectra recorded between 1 and 6 h. This band may be confidently assigned to a C=C stretching vibration resulting from the formation of alkenes during thermal stressing. Between 6 and 18 h the 1642 cm⁻¹ band decreases in intensity and there is only a minor component after 18 h in air at 425°C. After about 6 h of thermal stressing we observe other bands appearing at approximately 1600 cm⁻¹ which grow in intensity with increasing time from between 6 to 18h of thermal stressing. These bands are assigned to the ring stretching vibrations of aromatic compounds. Figure 41 clearly indicates

that during the thermal degradation of dodecane the formation of olefins occurs followed by subsequent cyclization and aromatization. The reader may wish to compare these results with the analogous jet fuel experiments (M. M. Coleman et. al , Energy and Fuels, 1992, 6(5) 535.). In the case of the dodecane experiments, aromatic species are directly derived from the parent hydrocarbon upon thermal stressing, whereas the "pure" jet fuel already contains aromatic species, which complicates interpretation.

Figure 42 shows the infrared spectra in the region 1550–1850 cm^{-1} of dodecane stressed with 5% benzyl alcohol. Immediately, one is struck by the presence and behavior of the band at 1710 cm^{-1} , which can be assigned to the carbonyl stretching vibration of benzaldehyde. The intensity of this band increases to a maximum after approximately 3 h of thermal stressing at 425°C, decreases somewhat at 6 h and is only a minor component at 12 h. Concomitant with these observations, we see that the band assigned to the C=C stretching vibration (1642 cm^{-1}) is detected at 1 h, rises to a maximum at about 6 h and is only a minor component at 18 h of thermal stressing. On comparing Figures 41 and 42 it is observed that the rise and fall of intensity of the band at 1642 cm^{-1} is retarded in dodecane in the presence of 5% benzyl alcohol. Finally, after about 6 h a band is detected at approximately 1695 cm^{-1} which is most probably associated with benzoic acid—the product of the oxidation of benzaldehyde.

Figure 43 shows the results of a quantitative analysis using the infrared band at 1642 cm^{-1} for dodecane neat (top) and dodecane with 5% benzyl alcohol (bottom). It is observed that in the absence of the additive the intensity of the olefinic band maximizes at 3 h of thermal stressing, whereas in the presence of the additive this band reaches a maximum after approximately 6 h of stressing; a retardation of about 3 h.

2. ^1H NMR Studies. Analogous studies to the infrared experiments were performed using ^1H NMR. Figure 44 shows the olefinic region of the neat dodecane. The spectra have been extensively scale expanded, but we qualitatively observed the formation of alkenes, which also maximize between 3 and 6 h. In the presence of benzyl alcohol (Figure 45) a maximum concentration is observed at six hours, which is consistent with infrared results. Also observed in the NMR spectra are sharp lines in the region 4.6 to 4.8 ppm which are attributed to benzyl alcohol and most probably to dibenzyl ether.

3. Gas Chromatographic Studies. Figure 46 shows the results obtained from a GC analysis of the amount of dodecane remaining after samples of pure dodecane and dodecane with 5% benzyl alcohol were stressed in air (top) and under nitrogen (bottom) as a function of time at 425° C. It is apparent from the plots that addition of 5% benzyl alcohol retards the degradation of dodecane and, unsurprisingly, the effect is more pronounced under nitrogen atmosphere. The products of benzyl alcohol degradation were identified clearly using GC

analysis. Figure 47 (a, b, c) shows the gas chromatogram of dodecane with 5% benzyl alcohol stressed for 3 h under 100 psi air. Identified are at ≈ 3 min benzene, ≈ 6 min toluene, ≈ 18 min benzaldehyde, ≈ 20 min dodecane, ≈ 21 min benzyl alcohol, and ≈ 44 min dibenzyl ether. All these compounds were confirmed using mass spectroscopy.

These studies have supported further experiments with deuterated dodecane which are currently being performed. Preliminary results are very encouraging and appear to offer mechanistic insights, that we will present in the next report.

2. Hydrogen-transferring Pyrolysis of Tetradecane—Enhancing High-Temperature Stability of Jet Fuels by H-Donors. (Contributed by Chunshan Song and Wei-Chuan Lai).

Introduction

Hydrogen-transferring pyrolysis reported here refers to the thermal decomposition of hydrocarbons in the presence of a hydrogen-transfer agent, or H-donor. The present work is a part of an on-going research program for developing advanced jet fuels thermally stable at high temperatures in the pyrolytic (400–450 °C) regime [Song et al., 1992a, 1993a; Lai et al., 1992]. This work is a continuation of a fundamental study that we initiated recently of high-pressure, long-duration pyrolysis of saturated hydrocarbons including the long-chain paraffins, alkylcyclohexanes, trans- and cis-steric isomers of decalin, as well as hydroaromatics such as tetralin [Song et al., 1992c], which have been identified as major components of either petroleum- or coal-derived jet fuels [Song and Hatcher, 1992]. One of the critical problems in developing thermally stable jet fuels for high-Mach aircraft is the thermal decomposition and formation of solid from hydrocarbon fuels in pyrolytic regime [Roquemore et al., 1989; Hazlett, 1991; Moler and Steward, 1989; Eser et al., 1992]. In studying the pyrolytic degradation of coal- and petroleum-derived 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 in inhibiting solid formation [Song et al., 1992a, 1993a].

Until recently, the major concerns of jet fuel stability only involved thermal oxidation stability and storage stability, because the current operating temperature of all the commercial and military jet fuels is limited to below 300 °C, where the fuel degradation is controlled by autoxidation reactions [Morris et al., 1988]. With the renewed interest of developing high-Mach aircraft, thermal stability at high temperatures has become more crucial. The relevant background information on the high-temperature thermal environments of the future jet fuels for high-Mach aircraft have been described in several recent papers [Roquemore et al., 1989; Lee and Niedzwiecki, 1989; Moler and Steward, 1989; Song et al., 1993a]. In a preceding

section we have discussed the characteristics of product distribution and reaction mechanisms for pyrolysis of n-tetradecane under comparable conditions. In this section we will report on 1) the results of detailed analysis of products from pyrolytic degradation of tetradecane; 2) effects of H-donors on the decomposition of n-tetradecane (n-C₁₄); 3) inhibiting effects of H-donors on the solid deposition from n-C₁₄ and a real jet fuel as well as an aromatic model compound, n-butylbenzene (n-BB); and 4) the mechanisms of the H-transferring pyrolysis of n-C₁₄, together with the effects of reactive compounds on the thermal reactions of H-donors.

While the temperature range for industrial pyrolysis processes is 600–900 °C [Willems and Froment, 1988], the bulk fuel temperature of interest for long-duration pyrolysis of jet fuels is in the range of 400–500 °C. The test temperature of 450°C (842 °F) used in this work is considered to be close to the anticipated high bulk fuel temperature for future high-Mach aircraft [Storch and Harrison, personal communication, 1992]. It should be noted that the development of advanced fuels for high-Mach flights requires the testing in long residence times in fuel systems to which the fuel is subjected to moderate to high heat loads, as well as the tests under conditions of very high heat flux at short residence times which fuels encounter in their passage through fuel struts and injectors. The earlier results of Hazlett et al. [1977,1991] and Frenkenfeld and Taylor [1980] on the effects of temperature apply to the short residence time (28 seconds) degradation in a flow tube. The results of the present work, however, are pertinent to the medium and long-duration pyrolytic degradation characteristics of jet fuels at high temperatures in the presence of H-donors which are components of coal-derived jet fuels. The experimental conditions used in this work 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 alkane pyrolysis work (vapor phase, low-pressure, flow reactor, short residence time).

Experimental

The reactants used in this work are Aldrich reagent-grade normal tetradecane, n-C₁₄ (MW: 198.4; bp: 252–254 °C; purity: 99+ %), tetralin (MW: 132.2; bp: 207 °C; purity: 99 %), trans-decalin (trans-D, MW: 138.3; bp: 187.3 °C; purity: 99 %), cis-decalin (cis-D, MW: 138.3; bp: 195.8 °C; purity: 99 %), decalin (mixture of cis and trans isomers; bp: 189–191 °C; purity: 99+ %), and n-butylbenzene (MW: 134.2, bp: 183.3 °C; purity: 99+ %). We also tested a real JP-8 jet fuel derived from petroleum (JP-8P), whose properties are described elsewhere [Lai et al., 1992; Song et al., 1992a]. The so-called hydrogen-donor compounds 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 25 mL 316 stainless steel microreactor. For hydrogen-transferring pyrolysis, the 5 mL mixture of

a compound or JP-8P jet fuel and a H-donor agent, usually 10% by volume unless otherwise mentioned, was transferred into the reactor. The pyrolysis was conducted at 450°C for 6–240 min 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 reactor pressure was monitored after the microautoclave was plunged in the sandbath. The gaseous products were analyzed by using GC with a packed column [Lai et al., 1992]. The liquid products were identified by capillary GC-MS and quantified by capillary GC. To make the quantification as reliable as possible, more than thirty pure compounds were used to calibrate the capillary GC responses of the liquid products, and more than ten pure compounds used to calibrate the GC responses of gaseous products. More analytical details may be found elsewhere [Lai et al., 1992; Song et al., 1993b].

Results and Discussion

1. Hydrogen-Transferring Pyrolysis of n-Tetradecane. Since closed reactors were used, the pressure changes with time are often characteristic of reactivity of hydrocarbons toward thermal decomposition. As shown in Figure 48, while the system pressure with tetralin, a hydrogen donor, almost remained constant, that with n-C₁₄ displayed a sharp increase after the initial heat-up. Adding tetralin considerably reduced the pressure increase during n-C₁₄ pyrolysis, especially in the first 30 min where the pressure with the 10% tetralin – 90% n-C₁₄ mixture was lower than with either n-C₁₄ or tetralin alone. This is indicative of the reduced formation of lighter products upon tetralin addition. Table 7 presents the detailed analytical results of products from pyrolysis of n-C₁₄ in the presence of tetralin. Adding tetralin affected not only the extent of decomposition, but also the distribution of products ranging from the lightest molecules such as methane to the heaviest products such as solid deposits.

Figure 49 shows the effect of tetralin on the n-C₁₄ conversion within the first 30 min. The n-C₁₄ conversion in the first 6 min is limited to ≤ 4 mol%. Measurement of the temperature inside the reactor has clearly shown that this period involves mainly heat-up from ambient to reaction temperature. After this heat-up period, n-C₁₄ conversion increased almost linearly with increasing residence time up to 30 min. Substantial inhibiting effect of tetralin on thermal decomposition reactions is apparent from Figure 49. One can quantify such an effect from Table I and Figure 49: adding 10 vol% of tetralin suppressed the decomposition of n-C₁₄, by about 68 % after 12 min of residence time (of reactor) at 450 °C [e.g., $(16.9-5.4)/16.9 = 68.0$ %], by about 66 % after 21 min, and by 37 % after 30 min.

Relative to the runs of n-C₁₄ alone, the H-transfer pyrolysis gave decreased yields of both alkanes and alkenes. The changes are small within the first 6 min because of the very low conversion, but become remarkable after 12 min. Surprisingly, the molar ratio of 1-dodecene

to n-dodecane increased dramatically, whereas the other 1-alkene/n-alkane ratios only rose slightly upon the addition of tetralin, as shown in Figure 50. For n-C₁₄ pyrolysis at 450°C, adding 10 vol % tetralin increased the 1-dodecene/n-dodecane ratio from 5.1 to 9.3 after 12 min, but that of 1-decene to n-decane increased to a much less extent, from 1.2 to 1.3 upon tetralin addition. The alkene/alkane ratio decreased with increasing time, and the differences between the values from pyrolysis and H-transfer pyrolysis become smaller. Thus in the 30 min run, adding tetralin increased the ratio of 1-dodecene to n-dodecane from 1.6 to 2.6, and that of 1-undecene to undecane from 0.5 to 0.6.

These results unambiguously show that the formation of n-dodecane decreased much more than that of 1-dodecene upon tetralin addition. This observation can be rationalized by considering the kinetics of elementary radical reactions. In the initial stage, the m-2 straight chain paraffinic product from C_mH_{2m+2} can only be formed from the β-scission of a primary radical 1-C_mH_{2m+1}• followed by H-abstraction. However, the m-2 olefinic product is produced from β-scission of a secondary radical, 4-C_mH_{2m+1}•. While adding H-donor has the potential to stabilize both types of radicals, as shown in Scheme VI, H-abstraction by primary radicals is preferred. This is because a secondary radical is more stable than a primary radical; H-abstraction by the former requires 2–3 kcal/mol more activation energy than by the latter [Allara and Shaw, 1980]. Therefore, the rate of H-abstraction by a primary radical is faster than that by a secondary radical.

Figures 51, 52, and 53 show the changes in product distribution upon addition of 10 vol % tetralin to n-C₁₄ after 12, 21 and 30 min, respectively. The effects of tetralin on product distribution patterns appear to be dependent upon the extents of n-C₁₄ decomposition or the residence time. At very low conversion (4 %), which corresponds to a 6 min residence time (RT) of the reactor, the effects of tetralin on product distribution are small. It appeared to have suppressed the alkene formation (Table 7) but the very low yields and low conversion (≤ 4 %) do not provide a reliable data base for further discussion. When the residence time is extended to 12 min, the presence of tetralin altered the pattern of product distribution, as shown in Figure 51. In the absence of a H-donor, there appeared a preferred formation of 1-pentene and 1-hexene from n-C₁₄ after 12 min. The preferential formation of 1-hexene has been attributed to a 1,5-shift isomerization of a primary radical generated from substrate molecule or a substrate radical followed by the β-scission; similarly, the preferential formation of 1-pentene has been attributed to a 1,4-shift isomerization of a primary radical followed by the β-scission [Song et al., 1993b]. If these pathways are correct, such isomerization should be selectively suppressed by adding H-donor, because H-abstraction by primary radicals is preferred. In fact this is the case. Adding tetralin strongly suppressed the preferential formation of 1-pentene and 1-hexene, giving a flat distribution pattern of C₃-C₁₁ 1-alkenes.

This trend essentially continued up to 21 min RT, as can be seen from Figure 52. With further increase in residence time, the peak carbon number of olefinic products shift from 5–6 towards 4 and finally towards 3, but using tetralin also retarded this shift (Figure 53, Table 7). It is also apparent from Table 7 and Figures 51–53 that formation of light alkanes, including methane, ethane and propane, from $n\text{-C}_{14}$ was suppressed most significantly by adding tetralin. The extent of decrease in CH_4 yields, relative to pure $n\text{-C}_{14}$ pyrolysis, also increased with increasing amount of tetralin added from 5 to 50 vol %. In addition, for the runs with 12–30 min RT, the yields of 1-alkenes from $n\text{-C}_{14}$ also decreased with increasing carbon-number from 5 to 13.

Based on the compositional differences of the products and the mechanisms of C_{14} pyrolysis discussed elsewhere [Song et al., 1993b], it seems that the alteration of product distribution pattern with tetralin is mainly due to its differentiation between different radicals, being more effective in stabilizing *pri*- $\text{R}^\bullet$ than the *sec*- $\text{R}^\bullet$, the latter being more stable than the former. In other words, *pri*- $\text{R}^\bullet$ can abstract hydrogen from tetralin more rapidly than *sec*- $\text{R}^\bullet$; this leads to decreased yields of both alkanes and alkenes but with increased ratio of alkene/alkanes upon tetralin addition in the short duration runs. The decreased yields of decomposition products are due to substantially reduced β -scission as a result of interruption of radical chain reaction by the H-donating action of tetralin. The possible reaction mechanisms are shown in Scheme VII.

The mechanisms shown in Scheme VII are our conceptual model accounting for the retardation of $n\text{-C}_{14}$ pyrolysis by tetralin. According to these mechanisms, H-donors strongly suppress any further reaction of the first radical formed from β -scission of a secondary substrate radical. Thus the chain propagation, the second-step β -scission as well as the isomerization of the primary radicals, is significantly inhibited. The overall reaction mechanism for the initial pyrolysis stage is characterized by an one-step β -scission of secondary radical followed by H-abstraction of the resulting primary radical. It is not difficult to answer the question as to why the primary radicals tend to undergo H-abstraction preferentially as compared to secondary radicals. The radical stability decreases in the order of tertiary > secondary > primary > $\text{CH}_3^\bullet$ radical. A secondary radical is more stable and hence its H-abstraction reaction requires 2–3 kcal/mol higher activation energy and proceeds at lower rate as compared to its corresponding primary radical [Allara and Shaw, 1980]. Most parent radicals are secondary radicals, but all of their β -scission reactions only generate primary radicals.

In long-duration pyrolysis, the effect of tetralin in suppressing $n\text{-C}_{14}$ conversion becomes smaller. This is because H-donors inhibit the radical-induced reactions but do not suppress the homolytic C–C bond cleavage. After 4 h, the major effects of H-donor appear to

be the inhibition of the formation of C_1 - C_4 hydrocarbon gases, as can be seen from Figure 54. Only small amounts of olefinic products remain after 240 min, with a peak centering at propylene, and most products are alkanes. The yields of C_1 - C_3 alkanes decreased with increasing amount of tetralin added. For comparison, Figure 55 gives the carbon number distribution of paraffinic products of n - C_{14} pyrolyzed at 450 °C for 6–480 min. Apparently, comparing Figure 54 with Figure 55 points to the remarkable retardation of thermal decomposition by using a hydrogen donor.

2. Inhibition of Solid Formation by Hydrogen Donors. One of the critical problems in developing thermally stable jet fuels is formation of solid deposits from hydrocarbon fuels in pyrolytic regime [Roquemore et al., 1989; Hazlett, 1991; Song et al., 1993a]. The present work on H-transferring pyrolysis also seeks to clarify whether and how the hydrogen-donors affect the solid-forming tendencies of jet fuel components. Figure 56 shows the inhibiting effect of tetralin on solid deposit formation from JP-8P fuel, n - C_{14} , and n -BB, respectively, at 450°C for 4 h. In the absence of H-donor, the amounts of deposits formed were 5.6 wt% from n -BB, 3.1 wt% from JP-8P, and 3.0 wt% from n - C_{14} . These figures are extremely large if one considers the deposit formation inside fuel lines in aircraft, because jet fuel loading is usually tens of tons. It is clear from Figure 56 that adding a small amount of tetralin significantly reduced the deposit formation from all these compounds. As for the efficiency of H-donor, adding 10 vol% tetralin to JP-8, n - C_{14} and n -BB reduced the formation of deposits by 90% (from 3.1 to 0.3 wt %), 77% (from 3.0 to 0.7 wt %) and 54% (from 5.6 to 2.6 wt %), respectively. The present results demonstrate that by taking advantage of H-transferring pyrolysis, hydrocarbon jet fuels can be used at high operating temperatures in pyrolytic regime with little or no solid deposition.

Multi-ring cyclic alkanes such as decalin can also serve as H-donors at high temperatures, although decalin is not as active as tetralin for inhibiting solid formation [Song et al., 1991c]. Table 8 shows that decalin can also suppress the deposit formation from JP-8P jet fuel, n - C_{14} and n -BB. In fact, adding both trans- and cis-D in 50 vol % almost eliminated solid formation from n - C_{14} , JP-8P, and n -BB. Since decalin and n - C_{14} are also representative components of coal- and petroleum-derived jet fuels, respectively, their mixture can also be viewed as a fuel blend. These results also account for the fact observed in previous work that the presence of significant amounts of C_{12} - C_{18} in coal-derived JP-8C did not cause remarkable solid formation [Song et al., 1992a, 1993a]. A practical implication from these results is that adding certain amounts of coal-derived fuel may enhance the high-temperature stability of petroleum-derived fuel. As discussed in previous papers [Song et al., 1992b, 1993b], the overall process for solid formation from paraffinic jet fuels appeared to be as follows:

Long-chain paraffins → alkenes → cycloalkenes → alkylbenzenes → polyaromatics → solids

It is apparent from Table 7 that the cyclization and aromatization reactions during n-C₁₄ pyrolysis are inhibited significantly in the presence of tetralin. Based on the foregoing, the enhanced stability of hydrocarbons and the reduced solid formation in H-transferring pyrolysis can be attributed to the stabilization of the reactive radicals via hydrogen-abstraction from H-donors such as tetralin, as shown in Scheme VIII. When hydroaromatics are not readily available or their concentrations become very low, the polycyclic hydrocarbons such as decalin can also act as hydrogen donors. The final product of such H-transfer reaction is naphthalene, and it is one of the major product from thermal stressing of samples containing either tetralin or decalin. H-donation from such compounds contributes mainly to inhibiting the radical reactions and suppressing solid formation, but the effectiveness of H-transfer is substantially higher with tetralin than with decalin, because the benzylic radical from tetralin is more stable.

3. Pyrolysis of Tetralin with and without Reactive Compounds. Table 9 presents the detailed results of products from tetralin pyrolysis. Tetralin is relatively stable when stressed alone at 450°C. The major products from pyrolysis of pure tetralin are 1-methylindan and naphthalene as well as a small amount of n-butylbenzene. We also noted the isomerization of cis-decalin to trans-decalin (both of them are present in tetralin originally as impurities, 0.36 mol%) and the increase in trans-decalin/cis-decalin ratio with residence time from 0.52 in 30 min, to 1.06 in 1 h and to 3.75 after 8 h. Figure 57 shows the temporal variations of the major products from tetralin. Even after 8 h pyrolysis at 450°C, the total gas products were still within 1 wt%, indicating the ring-opening cracking and subsequent dealkylation reactions were very limited with tetralin. It should also be noted that small amounts of CO and CO₂ were detected in the gas from tetralin. Detailed GC-MS and capillary GC analysis of the original reagent tetralin indicated the presence of 1.2 mol% of 3,4-dihydro-1-naphthaleneone, 0.6 mol% of 1,2,3,4-tetrahydro-1-naphthalenol, as well as 0.1% trans-decalin and 0.3% trans-decalin. Probably they were formed by oxidation during storage. However, the presence of these impurities had little effect in enhancing tetralin decomposition because of its radical scavenging ability.

However, in the H-transferring pyrolysis of n-C₁₄ and n-BB, the distribution of products from tetralin shows a significantly different pattern. As shown in Scheme IX, in the presence of reactive compounds, tetralin mainly undergoes dehydrogenation reaction to form naphthalene. For the mixtures of 10 vol% tetralin with reactive compounds such as n-C₁₄ or n-BB, the ring-contraction isomerization was enhanced slightly at 450°C for 30 min but

further increasing residence time increased mainly dehydrogenation. After 4 h, more than 90% of tetralin has been dehydrogenated in the case of its mixture and its isomerization was reduced significantly as compared to the run of itself. For 30 min runs, the radicals from n-BB were more active in dehydrogenating tetralin, although n-BB conversion was lower than that of n-C₁₄ under this condition. For the mixtures of 25 vol% tetralin with n-C₁₄, however, the yield of 1-methylindan from tetralin increased significantly after 4 h run, the value of which is close to that from pure tetralin.

These results clearly indicate that when the amount of H-donor tetralin is small (10 vol%), the reactive radicals generated from pyrolysis of n-C₁₄ and n-BB accelerate the tetralin dehydrogenation via H-abstraction, as shown in Scheme VIII, but such radicals do not promote the ring-contraction isomerization as significant as the dehydrogenation, as can be seen from Scheme IX. When more tetralin (25 vol%) is available, the radicals from n-C₁₄ also promote the isomerization, but such increase was not significant with the radicals from n-BB.

On the basis of the findings of Benjamin et al. (1979) and Franz et al. (1980), the isomerization proceeds mainly through the 2-tetralyl radical to form 1-indanylmethyl radical, as shown in Scheme X. In the presence of unstable compounds, the thermally generated reactive radicals can also lead the 2-tetralyl radical to dihydronaphthalene and subsequently naphthalene, as also shown in Scheme X. This explains why the dehydrogenation reaction of tetralin is dominant. When the H-donor concentration is relatively low, the radicals from n-C₁₄ and n-BB mainly abstract benzylic hydrogen to yield 1-tetralyl radical. In such case, the formation of 2-tetralyl radical is very limited and hence the isomerization is not very important. This also confirms that the reactions via 1-tetralyl radical shown in Scheme VIII are major pathways for hydrogen donation. When tetralin is present in high level, however, the probability for radicals to abstract hydrogens from 2-position increases. As a result, n-C₁₄ not only promotes tetralin dehydrogenation, but also enhances the isomerization to form 1-methylindan in the presence of excess tetralin, although the former is still the dominant reaction.

4. Some Practical Aspects. The present results are pertinent to pyrolytic degradation at high temperatures in the absence of air. The fuel degradation in real situations, of course, may incorporate both autoxidation reactions at low temperatures and pyrolytic reactions at high temperatures. Although we did not examine the autoxidation reactions under hydrogen-transfer conditions, some useful information has been generated in the past. Russell [1955] studied the oxidation of tetralin and cumene and found that small quantities of tetralin added to cumene would markedly lower the rate of oxidation, even though neat tetralin oxidized 10 times as fast as cumene at the same temperature and initiation rate [Taylor, 1969]. Similar

effects have been observed in other oxidation studies [Alagy, 1961; Alagy et al., 1959]. Taylor [1969] found that under thermal oxidation conditions (250°F) tetralin reduced deposits by more than 80% in air-saturated blends, although the H-donor property was not recognized and understood in earlier work. In fact, tetralin was one of the most effective inhibitors studied by Taylor (1969), presumably because it possesses four benzylic hydrogen atoms which inhibit cooxidation reactions involving hydrogen abstraction by peroxy radicals [Ingold, 1967; Frankenfeld and Taylor, 1980]. In deoxygenated fuels, tetralin was only slightly inhibitory at relatively low temperatures. More recently, Kubo [1991, 1992] has demonstrated that tetralin has radical scavenging ability in the presence of oxygen at both 50 °C and 350 °C.

Summary

Relative to the pyrolysis of pure paraffinic jet fuel components, two of the salient features of the hydrogen-transferring pyrolysis are the much lower rate of decomposition of the starting materials, and the substantially reduced amounts of solid deposits. Hydrogen donors such as tetralin are quite stable when stressed alone, but they act like radical scavenger by donating hydrogen to the radicals from reactive compounds. Therefore, the radicals from reactive compounds, via H-abstraction, enhance the dehydrogenation reaction of tetralin or decalin.

The results of H-transferring pyrolysis of reactive compounds in the presence of H-donors provided some very important information. Adding H-donors such as tetralin or decalin to the conventional jet fuel significantly reduced or even eliminated the formation of carbonaceous deposits at 450°C and decreased the extents of fuel decomposition and gas formation, which lead to substantial increase in the fuel stability. For runs at 450°C for 4 h, adding 10 vol% tetralin to JP-8, n-C₁₄ and n-BB reduced the formation of deposits by 94% (from 3.1 to 0.2 wt%), 77% (from 3.0 to 0.7 wt%) and 54% (from 5.6 to 2.6 wt%), respectively. The enhanced stability can be attributed to the stabilization of the reactive radicals via H-abstraction from tetralin or decalin type compounds, which contributes mainly to inhibiting the radical decomposition, cyclization, aromatization, and condensation reactions. These results clearly demonstrate that by means of hydrogen-transferring pyrolysis, hydrocarbon jet fuels can be used at high operating temperatures with little or no solid deposition.

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

1. A Structural Study of the Blind Canyon Coals (DECS-6 AND DECS-16) Using SolidState ^{13}C NMR Spectroscopy (Contributed by Lie Hou, Daniel McKinney, Jacqueline Bortiatynski, and Patrick Hatcher).

Coals rich in resinite are considered potential feedstocks for jet fuels, since resins consist of predominantly two-ring cycloparaffin structures. These cycloparaffins are linked to the side chains of these coals networks and can be cleaved in liquefaction processes. In an effort to optimize the liquefaction process, an adequate understanding of the structures of potential coal feed stocks is a necessary task. This section is a compilation of various NMR parameters that have been obtained for two coal samples using solid state ^{13}C NMR. The experiments include cross-polarization and magic-angle spinning (CPMAS), Bloch decay, dipolar dephasing and varied relaxation time experiments. The NMR parameters obtained from these experiments are used to structurally characterize the two potential coal feed stocks.

DECS-6 and DECS-16 were the coals chosen for this study, and they were obtained from the Penn State Coal Bank. The samples were collected in June of 1990 from the Upper Cretaceous Mesaverde group of the Blackhawk formation in Emery County, Utah. The results of proximate (as rec'd) and ultimate (dmmf) analyses and rank for the two samples are summarized in Table 10 and Table 11.

To insure that NMR data from a CPMAS experiment are quantitative, it is necessary to obtain a variety of relaxation data. Two conditions must be satisfied if quantitative data are to be obtained from a CPMAS experiment. First, the contact time (CT) used must be much greater than time required for polarization transfer between the carbons and the hydrogens

(T^{CH}), but it must also be much smaller than the spin-lattice relaxation time of protons in a rotating coordinate system (T_H^{1P}). Second, the spin-lattice relaxation times of the protons (T^{1H}) must be at least five times shorter than the delay between pulses. It is well known (1) that great care must be exercised to obtain quantitative data from solid state ^{13}C NMR on coal, since these materials have various macerals which differ in their molecular mobilities. In addition, paramagnetic centers concentrate in the aromatic portions of coal and directly affect the relaxation times for these types of carbons. Such factors will result in a broad range of T^{CH} and T_H^{1P} values that need to be applied to obtain quantitative NMR data for coals. Wilson et al. (2) reported that the T_H^{1P} 's for most coals range from 4 to 16 milliseconds, and Hatcher (3) has found that T^{CH} 's of coals are on the order of 0.1 to 2 milliseconds. Hence, the contact time and the pulse delay used in a CPMAS experiment must be carefully chosen in order to obtain quantitative results.

Appropriate values for T^{CH} and T_H^{1P} can be obtained from a variable contact time experiment (4). Figure 58 and Figure 59 are plots of the intensities of aromatic and aliphatic carbons of DECS-6 versus contact time (t^{CT}). The curves were fitted by equation (4):

$$M(t^{CT}) = M(0) \exp(-t^{CT}/T_H^{1P}) (1 - \exp(-bt^{CT}/T^{CH})) \quad (4)$$

where $M(0)$ is initial magnetization and $b = 1 - T^{CH}/T_H^{1P}$. The values of T^{CH} and T_H^{1P} for the aliphatic and aromatic carbons of DECS-6 and DECS-16 are listed in Table 12 and Table 13. T^{1H} was obtained inversely from the carbons (5). This method utilizes a 180° - t - 90° pulse sequence that is applied in the proton channel followed by a cross-polarization (CP) sequence in which the carbons obtain the encoded magnetization of their attached protons. Figure 60 and Figure 61 are graphs of the change in intensities of aromatic and aliphatic carbons versus inversion recovery time. The curves were then simulated by equation (5):

$$M(t) = M(0) - (0.8M(0) + M(0)) \exp(-t/T^{1H}) \quad (5)$$

where $M(0)$ is the equilibrium magnetization and 0.8 results from the influence of incomplete inversion. The T^{1H} 's obtained from the simulations for aliphatic and aromatic carbons of DECS-6 and DECS-16 were also put into Table 12 and Table 13. Based on the T^{CT} 's, T_H^{1P} 's and T^{1H} 's of DECS-6 and DECS-16, a one millisecond contact time and one second pulse delay were chosen for the CPMAS experiments of DECS-6 and DECS-16. Other important spectral parameters included a 3.5 KHz spinning speed and 18404 acquisition scans. The ^{13}C NMR spectra were obtained on a Chemagnetics M-100 NMR spectrometer with 100 MHz proton resonance frequency. Figure 62(a) is the CPMAS spectrum of DECS-6. A carbon

aromaticity of 0.62 was calculated from the spectrum. It is widely accepted that (1) ^{13}C NMR experiments on coal are more quantitative when the data is obtained using a Bloch decay which is one single pulse with a sufficient pulse delay between scans (greater than five times the carbon spin-lattice relaxation time). The Bloch decay experiment on DECS-6 required approximately 4127 acquisition scans and were obtained using a 90° pulse width (6 microsecond), with an 80 second pulse delay and is shown in Figure 62(b). The aromaticity was found to be 0.68 which is slightly larger than what had been obtained from the CPMAS experiment. The reason for the difference is that CPMAS will preferentially enhance the aliphatic signal due to inherent molecular motion of the carbons. The difference in aromaticities from these two methods suggests that even with optimal conditions for CPMAS experiments on DECS-6, the spectrum will still be somewhat distorted.

Because the NMR spectral data obtained using a Bloch decay pulse sequence provide the most quantitative distribution of different carbon functional groups, these spectra of DECS-6 and DECS-16 were simulated by using a curve-fitting program LAB CALC (Galactic Industries Co. 1990). Figure 63 is the simulated spectrum of DECS-6 which was used to quantitatively calculate the area of specific NMR bands for different functional groups in the Blind Canyon coals. The results are summarized in Table 14.

Dipolar dephasing experiments were also carried out on the Blind Canyon coals to provide additional structural information on the protonated and nonprotonated aromatic carbons. Plots of the areas of aromatic and aliphatic carbons of DECS-6 versus dephasing time (t_{dd}) are shown in Figures 64 and 65, respectively. A curve fit was achieved by using equation (6):

$$M(t_{dd}) = M_{0a} \exp(-t_{dd}^2 / 2T_{2a}^2) + M_{0b} \exp(-t_{dd} / T_{2b}) \quad (6)$$

where "a" and "b" represent protonated and nonprotonated carbons, respectively. M_{0a} and T_{2a} are the initial magnetization and the spin-spin relaxation times of protonated carbons (6), respectively. T_{2a} and T_{2b} for the aromatic and aliphatic carbons of the Blind Canyon coals were obtained from the curve-simulations and are summarized in Tables 12 and 13.

The ratios of the protonated aromatic carbons to total aromatic carbons (f_a^{aH}) for DECS-6 and DECS-16 were obtained from the curve fit, and they are found in Table 14. The proton aromaticity (H_{ar}) (7) is related to f_a^{aH} by equation (7):

$$H_{ar} = (C/H) f_a^{aH} f_a \quad (7)$$

where C/H is the organic carbon to hydrogen atomic ratio which can be obtained from elementary analysis and f_a is the carbon aromaticity. The calculated hydrogen aromaticities for DECS-6 and DECS-16 from the above equation are also found in Table 14.

The qualitative chemical characterization of DECS-16 appeared in a previous report (8). From a quantitative or qualitative standpoint DECS-6 and DECS-16 are very similar in their chemical characteristics. For example, the percents of the aromatic (70 %) and aliphatic carbons (30 %) are very similar, while the percents of oxygenated carbons are the same (15 %). The distribution of oxygen-containing functional groups for the two samples does differ. The distribution for the DECS-6 is as follows: 7% phenolic carbons, 3% carboxyl carbons, 2% carbonyl carbons and 3% oxygenated aliphatic carbons. The same functional groups are slightly different for the DECS-16 sample, since the phenolic carbons are 10%, the carboxyl content is 1 %, the carbonyl content is the same, and the oxygenated aliphatic carbons are 2%. The hydrogen distributions are also somewhat different for the two samples DECS-16 (83 %) contains more aliphatic hydrogens than DECS-6 (79 %). The hydrogen distribution is supported by the fact that DECS-16 has a slightly higher resinite content (5.11%) in comparison to DECS-6 (5%), and resinite is known to be rich in aliphatic hydrogen. For every aromatic ring, there are about 1.8 and 1.4 protonated carbons in DECS-6 and DECS-16, respectively. DECS-16 has twice the number of methylated aliphatic carbons as DECS-6.

These quantitative data obtained on the Blind Canyon coals will be used as a foundation for three-dimensional coal molecular models. Computer modeling of the Blind Canyon coals will be reported in a future report.

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2. Hydrogenation/Dehydrogenation Reactions of Rosin (Contributed by Richard Dutta)

Introduction

The development of high-performance jet aircraft has necessitated the development of fuel of high thermal stability. The fuel operating temperature is expected to increase significantly in the future due to the high temperature environment in high performance engines, aerodynamic heating, and higher heat loads from cooling aircraft system components. However, at high temperatures, pyrolysis reactions of certain components in the fuel become significant and result in the formation of gums and insoluble solids. These materials will reduce heat transfer efficiency, degrade valve performance and deposit solids in the fuel pipeline and in fuel combustor nozzles.

One of the most important factors controlling the high-temperature thermal stability of jet fuels is their chemical composition. Cycloalkanes are desirable components of advanced jet fuels because of their high thermal stability. If cycloalkanes can be produced in high yield by direct coal liquefaction, downstream processing of the product would be reduced. In order to obtain a high quality product, selection of a good feedstock is vital. Therefore, if cycloalkanes are to be produced from coal, it is reasonable to choose coals with high concentrations of these compounds already present.

The higher plants contain terpenoid substances commonly known as resins. These resins may polymerize on exposure to air, and the polymerization in situ in dead plants gives rise to the resinite maceral found in almost all coals. 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. Two major classes of resinite appear in coals. These are based on sesquiterpenoid and diterpenoid structures. Certain coals from Canada, the Far East and Australia contain diterpenoid resinites in high concentration. As well as appearing as resinite in coal, these compounds can also be found in large quantities by themselves. These are popularly known as amber. Western United States coals contain sesquiterpenoid resinite in high concentration (5%). This paper will deal with modeling of diterpenoid resinite structures, although the results obtained do have some relevance to sesquiterpenoid resinites. If the behavior of resinite under liquefaction conditions can be determined and understood, a highly efficient liquefaction system can be developed. Coals with high resinite concentration can be liquefied, and the cycloparaffinic products from resinite can be extracted into the oil fraction producing liquids that are thermally stable and could be a source of high quality jet fuel. However, because resinite is a complex mixture of polymerized compounds, 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 analogue of resinite structure and its hydrogenation-dehydrogenation behavior should give an insight into resinite liquefaction.

This section will discuss the aromatization/cracking/isomerization reactions of rosin compounds with various catalysts. The relevance of these reactions to resinite liquefaction and jet fuel production will be discussed.

Experimental

Rosin was hydrogenated under different conditions with NiMo/Al₂O₃, Ni-Y zeolite and ammonium tetrathiomolybdate. All reactions were carried out in standard microautoclave reactors, with a cold hydrogen pressure of 7 MPa. The products were analysed by GC/MS and quantified using heptadecane as an internal standard.

Results and Discussion

Figure 66 shows the concentration of reaction products and how they vary with temperature. 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 norabietatriene increases with increasing dehydrogenation of abietic acid. This increase also yields an increase in tetrahydroretene and retene in the reaction products. The concentration of alkylbenzenes triples in the products at the higher temperature. This can be accounted for by cracking of the saturated ring of the isopropyltetralin seen in the products formed 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 naphthalenes and benzenes are now being formed. These naphthalenes are cracking products of norabietatriene, tetrahydroretene, and other partially saturated 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 66 shows the

concentration of norabietatriene and tetrahydroretene 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 of 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 by cracking of the diterpenes in rosin. These compounds can form the "backbone" for subsequent hydrogenation to produce desirable cycloalkanes and tetralins. Unfortunately these cracking reactions occur at high temperatures, 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 will give rise 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; i.e. 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 forwards".

Figure 67 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 norabietatriene and tetrahydroretene. 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 tetrahydroretene is being hydrocracked. 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 68 and 69). Figure 68 shows the dehydrogenation pathway of abietic acid. Figure 69 deals with the possible route of cracking of the 3-ring compounds.

In order to establish the optimum conditions for a temperature-staged catalytic hydrogenation, the product distribution of rosin hydrogenation was investigated using three catalysts: NiMo/Al₂O₃, Ni-Y (zeolite), and ammonium tetrathiomolybdate (ATTM).

Figure 70 shows a histogram of the product distribution of rosin hydrogenation with various catalysts. (reaction temp. 400°C, reaction time 60 min.). All three of the catalysts caused a major reduction in the concentration of retene. ATTM did not crack the tricyclic compounds in rosin. In fact, it can be seen that the thermal run (no catalyst) produced more benzenes than the run with ATTM. This can be explained by the formation of dehydroabietane in the ATTM experiment. This compound is more stable than norabietatriene, due to the methyl group substitution of the carboxyl group. Therefore, dehydroabietane does not crack and shows less tendency to dehydrogenate. Because of the low hydrocracking effectiveness of ATTM it was decided not to continue with this catalyst in this investigation. Supported NiMo shows good hydrocracking effectiveness and the Ni-Y catalyst shows an even greater cracking capability. This was not surprising, due to the fact that zeolite catalysts are known in the petroleum industry for their excellent hydrocracking effectiveness. This preliminary investigation into catalytic reactions of rosin led into a more detailed look at how product distribution would vary with time. This would help in determining the best temperature program for the two stage reaction postulated previously.

Figure 71 shows the product distribution vs time for rosin hydrogenation with NiMo at 450°C. Three major points arise from this graph:

- 1) From 5 to 60 minutes, there is no overall increase in retene, but after 20 minutes methylphenanthrene is formed by dehydrogenation/dealkylation of tetrahydroretene.
- 2) The major cracking reactions occur after 10 minutes. Secondary cracking of naphthalenes to benzenes occurs after 20 minutes. This can be seen by the increase in concentration of benzenes after 20 minutes but naphthalenes show a "slowing down" of formation.
- 3) After 40 minutes there is a maximum in the benzenes concentration. This could be explained three ways—formation of gases, coking of the catalyst, or both. The appearance of methylphenanthrene tends to support the latter explanation.

Figure 72 shows a more detailed look at the benzene and naphthalene fraction of the products. 1-Methyl-4-isopropylbenzene (p-cymene) reaches a maximum in concentration at 40 minutes. Toluene increases slowly throughout the reaction times. The isopropyl group is quite stable but will be cleaved after 40 minutes at 450°C. This could also explain the decrease in benzenes concentration seen in Figure 71. This is due to C₂-C₃ hydrocarbon

gases being produced by cleavage of side chains. Isopropyltetralin reaches a maximum at approximately 30 minutes. The disappearance of isopropyltetralin is simultaneous with the increase in concentration of methylindene. This is due to dealkylation/isomerisation of isopropyltetralin, thus:

As mentioned in the introduction, this work does have some application to sesquiterpenoid resinite. The proposed pathway of dealkylation to tetralin would probably occur in sesquiterpenoid structures. The isomerisation reaction could probably be controlled by tailoring the reaction temperature, and the possibility of producing decalin is good. Investigations into reactions of sesquiterpenoid resinites will be the subject of a later report.

Figure 73 shows the product distribution of rosin hydrogenation vs time with Ni-Y catalyst at 450°C. It can be seen that after 10 minutes of reaction, the tricyclic compounds in rosin have almost totally been cracked. Benzenes, naphthalenes and indenes are produced in high concentration and continue to increase up to 60 minutes of reaction. Figure 74 shows a more detailed look at the benzenes, naphthalenes and indenes in the reaction mixture. Isopropyltetralin is completely cracked/dealkylated and isomerized after 60 minutes. The isomerisation reaction seems to be the major cause of loss of isopropyltetralin. This can be seen by the simultaneous increase of dihydromethylindene. p-Cymene is dealkylated to toluene after 10 minutes of reaction.

In order to find a relationship between the cracking of tricyclic compounds and the appearance of mono- and bicyclic compounds, a plot of the ratio of 3-ring/1+2 ring compounds is shown in Figure 75. It can be seen that Ni-Y is the most effective hydrocracking catalyst. The maximum at 20 minutes is probably due to secondary cracking of side chains producing gases. This would cause a decrease in the calculated ratio.

Conclusions

Diterpenoid compounds can be successfully hydrogenated and cracked to jet fuel compounds using NiMo and Ni-Y catalysts. With careful tailoring of the process temperature and time of reaction, high quality distillate could be obtained. A temperature-staged reaction with optimum conditions chosen from the plots of product distribution could yield maximum

concentration of cycloalkanes and hydronaphthalenes. Fully aromatic compounds would be kept to a minimum. Diterpenoids are the most common resins in the geosphere. As well as appearing in some coal resinites, they can be found as ambers or as modern pine resins, e.g. rosin. Their chemical properties can be used in developing high-quality fuels, either by direct hydrocracking or as a blending additive in a coal liquefaction process. Some of the reactions occurring in rosin hydrocracking (dealkylation/isomerisation) could be useful in determining the best way to study the liquefaction behavior of sesquiterpenoid resinites, e.g. as found in some Utah coals.

3. Bimetallic Dispersed Sulfide Catalysts from Organometallic Clusters for Coal Liquefaction (Contributed by Chunshan Song and Derrick Parfitt)

Introduction

This work is a part of our on-going program for developing advanced jet fuels thermally stable at high temperatures. Our recent work has demonstrated that, in the pyrolytic regime, the gross hydrocarbon makeup of jet fuels plays a key role in determining fuel degradation; coal-derived fuels are rich in cycloalkanes and are therefore inherently more stable and superior for high temperature applications [1]. This has led to the present work as an attempt to explore novel catalysts for producing cycloalkane-rich liquid fuels, in particular jet fuels, from coal through hydrogenation or hydrol liquefaction.

It has been recognized recently that dispersed catalysts are superior to supported catalysts for primary hydrol liquefaction of coal. Because most active catalysts of interest (e.g., MoS_2) are insoluble in common solvents, the desire to achieve better dispersion leads to the strategy of using a soluble precursor that can be dispersed on to coal surface from its solution. The precursor may not itself be active, but it transforms at elevated temperatures into an active catalyst. Both inorganic salts of transition metals [2,3] and organometallic compounds such as metal carbonyls have been tested as precursors for dispersed catalysts, mostly MoS_2 [4-7]. Some recent work on multicomponent catalysts has involved the mixture of two or more inorganic salts [8-11]. However, little work on bimetallic dispersed sulfide catalysts for coal liquefaction has appeared.

The present work is concerned with organometallic precursors which can directly produce bimetallic sulfides upon thermal decomposition. Related to this work are two important general observations from previous investigations: 1) there could be synergistic effects between two different transition metal compounds [2,8,9] and, 2) for a given metal, an organometallic precursor may be better than an inorganic one for coal liquefaction [12,13]. From the recent book on metal clusters by Mingos and Wales [14], it seemed to us that

highly active bimetallic catalysts may be prepared from the "thiocubane" clusters containing two transition metals such as Co and Mo in a single molecule. Two different metals bound together in a single cluster 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. Recently, Chianelli et al. [15] and Halbert et al. [16] have used the unsupported sulfides from bimetallic complexes to study the promotional effects of Co on MoS₂ for hydrodesulfurization (HDS). They have shown that the CoMo sulfide catalysts from some organometallic precursors exhibit greatly improved activity for HDS. In this communication we wish to report on a potential bimetallic dispersed catalyst system for coal liquefaction from thiocubane cluster.

Experimental

Reagent-grade Mo(CO)₆ and Co₂(CO)₈ were used as the primary starting materials. We synthesized three Mo-Co bimetallic thiocubane clusters, including Mo₂Co₂S₄(S₂CNEt₂)₂(CH₃CN)₂(CO)₂, Mo₂Co₂S₄Cp₂(CO)₂, and Mo₂Co₂S₄(Cp')₂(CO)₂, in which Et, Cp and Cp' represent the ethyl group, cyclopentadiene, and pentamethylcyclopentadiene, respectively. For convenience, we will refer to these three clusters as MoCo-TC1, MoCo-TC2, and MoCo-TC3, respectively. The method of Halbert et al. [17] was used for synthesizing MoCo-TC1, and that of Brunner and Watcher [18] for MoCo-TC3. We prepared MoCo-TC2 using the same procedure for MoCo-TC3 but with a modification of the starting material for the ligand. For comparative examination, a trianionic compound (PPh₄)₃Co(MoS₄)₂, designated as MoCo-S, was also synthesized as a bimetallic sulfide complex based on the procedure of Pan et al. [19].

For catalytic activity tests, we used a Montana subbituminous coal, which is one of the U.S. Department of Energy Coal Samples (DECS-9) stored under argon atmosphere in the Penn State/DOE Coal Sample Bank. DECS-9 (<60 mesh) has the following composition: 76.1% carbon, 5.1% hydrogen, 0.9% nitrogen, 0.3% organic sulfur, and 17.5% oxygen on a dry and mineral matter free (dmmf) basis. The catalyst precursors were dispersed on to the coal (predried at 100°C in vacuum) by the incipient wetness impregnation method using organic solvents, followed by vacuum drying at 100°C for over 2 h to remove the impregnating solvent. The loading for the bimetallic thiocubanes was 0.5 wt% of Mo on dmmf coal. When the metal carbonyls Mo(CO)₆ and Co₂(CO)₈ were used, the loading was 0.5 wt% for Mo and 0.3 wt% for Co metal based on dmmf coal.

The coal liquefaction was carried out in 25 mL microautoclaves in a fluidized sandbath at 400 or 425°C for 30 minutes under an initial (cold) H₂ pressure of 7 MPa (1000 psi). Each reaction used approximately 3 g dried coal and 3 g of 1-methylnaphthalene as the

reaction solvent. After the reaction, the gaseous product was vented, and the liquid and solid products were separated by sequential Soxhlet extraction into oil (hexane soluble), asphaltene (toluene soluble but hexane insoluble), preasphaltene (THF soluble but toluene insoluble) and residue [20,21]. In general, the experimental errors were within ± 2 wt% for conversion, and the average data from two or three runs are reported here.

Results and Discussion

Table 15 shows the results of liquefaction of the Montana subbituminous coal at 400°C for 30 min. We first prepared and tested MoCo-TC1, which has a cubane-like structure as shown in Figure 76 and was first synthesized and used recently by Halbert et al. [16,17] in preparing a 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 non-catalytic run by 14 wt%, but did not improve oil formation to any significant extent. It seems that the acetonitrile solvent is not good for catalyst impregnation. More importantly, the dithiocarbamate and acetonitrile ligands in MoCo-TC1 seem to poison the resulting catalyst under the conditions employed. This consideration prompted us to prepare the thiocubane which contains no nitrogen in the ligands, leading to the synthesis of MoCo-TC3 using the published method of Brunner and Watcher [18], and subsequently the synthesis of MoCo-TC2 using the same procedure but replacing C₅Me₅ with a simpler and cheaper C₅H₅ ligand. Therefore, the basic differences between these three thiocubanes are the type of ligands bound to the Mo, as indicated in Figure 76.

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 is used as the impregnating solvent. THF is known to be a better swelling solvent than toluene and using THF for impregnation of metal carbonyls has been shown to increase the conversion of Wyodak subbituminous coal due to improved metal dispersion [22]. Surprisingly, the catalytic liquefaction using MoCo-TC2 gave both higher oil yields and total conversion when toluene was used rather than THF for precursor impregnation.

The structure and ligands of MoCo-TC3 and MoCo-TC2 are of the same nature, except that pentamethylcyclopentadiene ligand in MoCo-TC3 is replaced by cyclopentadiene in MoCo-TC2. In an attempt to examine the role of bonding between Co and Mo, we further tested Co(MoS₄)₂³⁻ which has a distinctly different structure than the above-mentioned thiocubanes, as can be seen from comparison of Figure 77 with Figure 76. The results in

Table 15 reveal that MoCo-S is more active than MoCo-TC1, comparable (after further purification) to MoCo-TC3, but is less active compared to MoCo-TC2. A technical problem with MoCo-S is its air-sensitive nature: it decomposes during storage even in a refrigerator. Overall, the order of catalytic activity of the precursors appears to be MoCo-TC2 > MoCo-TC3 $\geq$ MoCo-S > MoCo-TC1. Since Mo(CO)₆ and Co₂(CO)₈ were used for synthesizing the bimetallic thiocubanes, we also tested these starting materials as precursors. They did show good catalytic effects in promoting coal conversion and oil yield when compared to MoCo-TC1. However, MoCo-TC2 and MoCo-TC3 are much better precursors than the Mo and Co carbonyls (Table 15) as well as their combinations.

Since the precursors may not be very active by themselves, their decomposition at low temperature, which could serve as an in-situ activation/generation of the active catalyst, may contribute to more effective hydrogenation of reactive fragments and aromatics at high temperature. Therefore, we also examined the influence of in-situ pretreatment at 200°C for 15 min. Our results clearly show that such pretreatment in the presence of MoCo-TC2 (or TC3) is beneficial and contributes to substantially increased coal conversion and oil yield, especially at higher reaction temperature (425 °C). However, when the metal carbonyls were used, neither conversion nor oil yield increased upon such an in-situ pretreatment. This comparison suggests that an active catalyst can be formed from MoCo-TC2 and MoCo-TC3 upon heat treatment at relatively low temperatures.

By combining the information in Table 15 and Figures 76 and 77, 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 comparable to that of MoCo-TC3 at 400°C. In MoCo-S, the Co and Mo are bonded through sulfur-bridge bonding (Figure 77), but in MoCo-TC2 or TC3, there are direct metal-metal bonds between Co-Mo, Co-Co, and Mo-Mo (Figure 76) in addition to the sulfur bridges. The differences between the three thiocubanes clearly indicate the importance of ligand type; the superiority of MoCo-TC2 over MoCo-S may suggest the importance of direct metal-metal bonding. The solvents used for loading the precursors are also influential. Both toluene and THF were tested for impregnating MoCo-TC2 but toluene solvent seems to be better in terms of higher oil yield. The solubilization of different bimetallic precursors often requires different solvents; the optimum solvent and method for loading catalyst precursors are not known yet.

Summary

In summary, the 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 by evaporation and vacuum drying. Among the M-M' type precursors tested, Mo-Co thiocubane, $\text{Mo}_2\text{Co}_2\text{S}_4(\text{Cp})_2(\text{CO})_2$ [Cp = cyclopentadiene] impregnated onto coal from toluene, generated in-situ the best catalyst (MoCo-TC2) for coal liquefaction. The performance of the MoCo-TC2 catalyst was further enhanced by using an in-situ thermal pretreatment.

We realize that the bimetallic catalysts reported in this work would be rather expensive for use in an industrial process. However, the knowledge derived from this work on the dependence of catalyst activity on the structure of the bimetallic precursor and fundamental chemistry are very important for the development of novel catalysts and advanced catalytic processes. Another potential application of the precursors reported in this paper is the preparation of supported Co-Mo catalysts which are usually prepared from inorganic salts [23]. Some of the bimetallic precursors will be used for preparing supported hydrotreating catalysts for more efficient upgrading of coal liquids as well as residual oils to high quality gasoline, jet fuels and diesel fuels.

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APPENDIX 1
TABLES

Table 1. Yields (mol%) of Major Compounds in Liquid Products

Compound Name	1 hr			4 hr			8 hr		
	400	425	450	400	425	450	400	425	450
Butane + Butene	0.52	4.99	5.67	3.97	8.69	7.45	5.58	7.50	6.73
Pentane + Pentene	0.58	4.00	5.90	3.84	8.85	6.55	5.71	7.19	4.89
2-Methylpentane	0.00	0.00	0.00	0.00	0.16	0.41	0.00	0.54	0.13
Hexane	2.82	14.00	14.90	12.90	20.00	9.57	16.90	15.90	4.80
2 or 3-Hexene	0.00	0.27	0.62	0.24	0.73	0.31	0.51	0.67	0.00
Methylhexane	0.00	0.11	0.46	0.09	0.87	0.80	0.31	0.75	0.90
Heptane	0.06	0.87	1.91	1.15	3.19	1.46	2.96	2.81	0.50
1-Heptene	3.29	6.46	3.13	5.00	1.41	1.13	2.99	1.16	0.79
2-Heptene	0.15	0.85	0.81	1.21	0.40	0.10	1.19	0.33	0.00
3-Heptene	0.10	0.47	0.37	0.57	0.24	0.06	0.53	0.60	0.00
Methylcyclohexane	0.04	0.49	1.04	0.49	1.13	0.88	0.92	1.07	0.51
Ethylcyclopentane	0.00	0.19	0.46	0.21	0.51	0.35	0.46	0.54	0.16
Benzene	0.00	0.33	0.93	0.24	1.12	1.69	0.55	1.66	2.37
Octane	0.03	0.42	0.86	0.42	0.94	0.47	0.90	0.70	0.12
Toluene	5.28	31.90	49.80	31.8	58.20	54.30	51.30	55.4	54.10
Nonane	0.03	0.44	0.66	0.45	0.79	0.21	0.87	0.46	0.04
3-Ethylhexane	0.00	0.00	0.24	0.13	0.28	0.00	0.33	0.16	0.00
Ethylbenzene	0.50	6.10	20.30	6.77	22.30	28.2	15.00	27.5	28.70
Decane	0.00	0.27	0.36	0.30	0.41	0.09	0.51	0.21	0.00
Xylene	0.00	0.00	0.15	0.00	0.16	0.35	0.00	0.28	0.43
Styrene	1.06	1.82	0.84	0.78	0.23	0.17	0.29	0.12	0.13
Isopropylbenzene	0.00	0.54	2.94	0.91	4.10	4.34	2.77	4.97	4.02
n-Propylbenzene	0.21	1.92	4.12	1.81	4.61	4.00	3.67	4.67	2.95
Allylbenzene	0.08	0.24	0.36	0.13	0.32	0.00	0.20	0.00	0.00
C3-Benzene	0.00	0.00	0.00	0.00	0.00	0.56	0.00	0.56	0.71
Undecane	0.00	0.00	0.14	0.14	0.18	0.03	0.23	0.08	0.00
Isobutylbenzene	0.00	0.12	0.31	0.11	0.38	0.40	0.28	0.43	0.33
s-Butylbenzene	0.00	0.12	0.49	0.17	0.71	0.44	0.59	0.78	0.20
Methylstyrene	0.13	0.63	0.35	0.31	0.12	0.10	0.12	0.00	0.09
Methylstyrene	0.00	0.13	0.18	0.08	0.07	0.09	0.06	0.21	0.11
C4-Benzene	0.00	0.00	0.00	0.07	0.00	0.00	0.04	0.00	0.00
C4-Benzene	0.00	0.01	0.05	0.01	0.06	0.07	0.00	0.09	0.06
C4-Benzene	0.00	0.00	0.03	0.00	0.04	0.03	0.00	0.05	0.03
n-Butylbenzene	0.40	2.83	3.69	2.51	2.97	0.93	3.46	1.79	0.35
C4-Benzene	0.06	0.14	0.09	0.08	0.06	0.07	0.05	0.08	0.09
Indan	0.00	0.00	0.16	0.05	0.17	0.20	0.11	0.21	0.22
C5-Benzene	0.00	0.00	0.29	0.00	0.30	0.10	0.00	0.19	0.03
C5-Benzene	0.00	0.00	0.00	0.19	0.00	0.00	0.39	0.14	0.00

Dimethylstyrene	0.00	0.00	0.10	0.00	0.00	0.21	0.07	0.25	0.21
5-Methyldodecane	0.02	0.00	0.00	0.18	0.00	0.00	0.20	0.00	0.00
n-Pentylbenzene	0.29	1.91	2.20	1.87	1.95	0.41	2.56	1.03	0.10
2,6,6-Trimethyldodecane	0.02	0.14	0.09	0.17	0.09	0.05	0.17	0.03	0.04
1,3-Dimethylbutylbenzene	0.00	0.15	0.21	0.22	0.21	0.06	0.30	0.13	0.06
1-Pentenylbenzene	0.06	0.19	0.14	0.13	0.06	0.00	0.09	0.02	0.00
nC6-Benzene	0.15	0.64	0.70	0.64	0.61	0.10	0.84	0.28	0.03
Naphthalene	0.00	0.54	1.84	0.49	1.67	2.38	1.00	2.32	2.74
1-Propylpentylbenzene	0.31	0.69	0.36	0.93	0.32	0.00	0.78	0.11	0.00
1-Ethylhexylbenzene	0.03	0.11	0.07	0.17	0.10	0.00	0.19	0.04	0.00
n-Heptylbenzene	0.10	0.42	0.41	0.51	0.30	0.00	0.56	0.11	0.00
3-Methyl-4-pentylbenzene	0.00	0.17	0.26	0.13	0.21	0.00	0.18	0.13	0.00
1-Methylheptylbenzene	0.50	1.20	0.60	1.59	0.49	0.04	1.35	0.14	0.00
2-Methylnaphthalene	0.00	0.00	0.25	0.00	0.25	0.43	0.00	0.47	0.61
C8-Benzene	0.06	0.36	0.19	0.24	0.10	0.00	0.17	0.04	0.00
1-Methylnaphthalene	0.00	0.18	0.70	0.24	0.70	0.89	0.51	1.19	1.02
n-Octylbenzene	88.20	37.30	13.70	44.00	6.13	0.60	19.50	1.12	0.01
Higher Alkylbenzene	0.00	0.15	0.00	0.23	0.09	0.00	0.26	0.00	0.00
Methylnaphthalene	0.00	0.02	0.07	0.00	0.05	0.11	0.00	0.15	0.17
Biphenyl	0.00	0.11	0.40	0.00	0.35	0.61	0.20	0.44	0.89
Methylbiphenyl	0.00	0.10	0.21	0.00	0.17	0.07	0.25	0.12	0.04
Methylnaphthalene	0.00	0.00	0.10	0.00	0.00	0.12	0.07	0.11	0.14
Methylnaphthalene	0.00	0.00	0.10	0.00	0.00	0.10	0.00	0.11	0.15
Methylnaphthalene	0.00	0.05	0.00	0.00	0.10	0.00	0.00	0.17	0.00
1-Octenylbenzene	0.16	0.35	0.25	0.49	0.16	0.00	0.45	0.00	0.00
C9-Alkylbenzenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Methylbiphenyl	0.00	0.00	0.11	0.00	0.13	0.15	0.09	0.13	0.24
Methylbiphenyl	0.00	0.00	0.26	0.00	0.27	0.36	0.17	0.32	0.56
Methylbiphenyl	0.00	0.00	0.13	0.00	0.12	0.15	0.12	0.13	0.23
Dimethylbiphenyl	0.00	0.00	0.09	0.00	0.09	0.08	0.09	0.09	0.13
Bibenzyl	0.00	0.11	0.18	0.10	0.16	0.04	0.18	0.09	0.06
C9-Benzene	0.05	0.11	0.00	0.11	0.00	0.00	0.08	0.00	0.00
Dimethylbiphenyl	0.00	0.00	0.00	0.00	0.12	0.10	0.00	0.12	0.17
Fluorene	0.00	0.00	0.00	0.00	0.03	0.10	0.00	0.07	0.21
Methylfluorene	0.00	0.00	0.00	0.00	0.04	0.06	0.00	0.08	0.09
Dimethylbiphenyl	0.00	0.00	0.00	0.00	0.08	0.07	0.00	0.08	0.10
Higher Alkylbenzene	0.15	0.38	0.14	0.32	0.04	0.00	0.10	0.02	0.00
Higher Alkylbenzene	0.02	0.16	0.11	0.11	0.05	0.00	0.09	0.00	0.00
Higher Alkylbenzene	0.09	0.14	0.00	0.24	0.00	0.00	0.08	0.00	0.00
Phenylnaphthalene	0.00	0.00	0.00	0.00	0.000	0.04	0.00	0.04	0.07
Phenylnaphthalene	0.00	0.00	0.02	0.02	0.04	0.07	0.03	0.05	0.12
Pyrene	0.00	0.03	0.04	0.03	0.03	0.04	0.03	0.04	0.07
Phenanthrene	0.00	0.00	0.04	0.00	0.03	0.07	0.00	0.06	0.18
Anthracene	0.00	0.00	0.03	0.00	0.03	0.03	0.00	0.04	0.05

Table 2. Products from n-Tetradecane Pyrolysis at 450°C under 0.69 MPa N₂ (Cold)

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	
Conversion (mol %)	3.98	16.92	31.68	53.33	70.27	90.63	97.08	99.16
Yields (mol %) ^b								
Hydrogen (H ₂)				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
Isobutane				0.03	0.26	0.88	1.45	1.97
n-Butane (n-C ₄)	0.35	2.02	4.31	8.41	7.49	16.18	17.62	21.08
1-Butene	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	
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	
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	
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			
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		
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			
n-Tetradecane (n-C ₁₄)	96.02	83.08	68.32	46.67	29.73	9.37	2.92	0.84
1-Tetradecene		0.02	0.14	0.21				
n-Pentadecane (n-C ₁₅)	0.08	0.14	0.24	0.36	0.42	0.23		
n-Hexadecane (n-C ₁₆)		0.06	0.16	0.26	0.29	0.12	0.06	
n-Heptadecane (n-C ₁₇)		0.04	0.11	0.17	0.16	0.04		
n-Octadecane (n-C ₁₈)	0.13	0.13	0.15	0.18	0.13	0.01		
n-Nonadecane (n-C ₁₉)		0.02	0.07	0.09				
n-Eicosane (n-C ₂₀)		0.02	0.06	0.07				
n-Henicosane (n-C ₂₁)		0.02	0.04	0.05				
n-Docosane (n-C ₂₂)		0.01	0.03	0.04				
n-Tricosane (n-C ₂₃)		0.01	0.02	0.03				
Methylcyclopentane		0.06	0.20	0.69	2.98	2.84	2.72	4.22
C ₂ - to C ₄ -cyclopentanes					0.42	0.59	0.80	0.79
Dimethylcyclopentene					0.47	0.42	0.12	0.43
Methylcyclohexane		0.09	0.30	0.81	2.11	3.07	2.35	3.06
C ₂ - to C ₃ -cyclohexanes		0.05	0.27	0.90	3.57	3.73	3.27	2.47
Benzene					0.28	0.65	0.70	1.19
Toluene				0.19	0.91	2.96	4.62	4.89
C ₂ - to C ₆ -benzenes				0.25	3.31	10.87	16.07	17.27
Indane						0.25	0.34	0.36
C ₁ - to C ₃ -indanes						1.20	2.30	2.58
C ₀ - and C ₁ -tetralins							0.04	0.13
Naphthalene						0.25	0.58	0.53
C ₁ - to C ₄ -naphthalenes						1.32	2.37	3.63
Other Polyaromatics						0.03	0.24	0.47
Solid deposits (wt%)						1.0	3.0	4.7

a) Pyrolysis of 5 mL of n-tetradecane in 25 mL reactors plunged into the sandbath preheated to 450 °C.

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

Table 3. Arrhenius Parameters for Elementary Reactions of Some Radicals

No.	Reactant	Reactant	Product	Product	$\log[A]^a$	E	$\log [k]^b$	Sources
	A	B	A	B		kcal/mol		
1	n-C ₅ H ₁₂		→ 1-C ₄ H ₉ •	+ CH ₃ •	17.5	85.5	-9.2	(S1)
2	n-C ₅ H ₁₂		→ 1-C ₃ H ₇ •	+ C ₂ H ₅ •	17.1	81.6	-8.4	(S1)
3	n-C ₆ H ₁₄		→ 1-C ₄ H ₉ •	+ C ₂ H ₅ •	16.8	81.9	-8.8	(S1)
4	n-C ₆ H ₁₄		→ 1-C ₃ H ₇ •	+ 1-C ₃ H ₇ •	16.5	81.9	-9.1	(S1)
5	n-C ₆ H ₁₄		→ 1-C ₅ H ₁₁ •	+ CH ₃ •	16.8	85.4	-9.9	(S1)
6	n-C _m H _{2m+2}		→ 1-C _n H _{2n+1} •	+ 1-C _i H _{2i+1} •		81-82		(S3), m ≥ 4, n ≤ 22
7	n-C _m H _{2m+2}		→ 1-C _n H _{2n+1} •	+ CH ₃ •		85-86		(S3), m ≥ 4, r
8	H	+ n-C ₄ H ₁₀	→ H ₂	+ 1-C ₄ H ₉ •	11.1	9.7	8.1	(S1)
9	H	+ n-C ₄ H ₁₀	→ H ₂	+ 2-C ₄ H ₉ •	11.1	7.7	8.7	(S1)
10	CH ₃ •	+ n-C ₄ H ₁₀	→ CH ₄	+ 1-C ₄ H ₉ •	8.6	11.4	5.0	(S1)
11	CH ₃ •	+ n-C ₄ H ₁₀	→ CH ₄	+ 2-C ₄ H ₉ •	8.9	9.5	5.9	(S1)
12	C ₂ H ₅ •	+ n-C ₄ H ₁₀	→ C ₂ H ₆	+ 1-C ₄ H ₉ •	8.5	12.3	4.6	(S1)
13	C ₂ H ₅ •	+ n-C ₄ H ₁₀	→ C ₂ H ₆	+ 2-C ₄ H ₉ •	8.0	10.4	4.8	(S1)
14	1-C ₃ H ₇ •	+ n-C ₄ H ₁₀	→ C ₃ H ₈	+ 1-C ₄ H ₉ •	8.5	12.3	4.6	(S1)
15	1-C ₃ H ₇ •	+ n-C ₄ H ₁₀	→ C ₃ H ₈	+ 2-C ₄ H ₉ •	8.0	10.4	4.8	(S1)
16	2-C ₃ H ₇ •	+ n-C ₄ H ₁₀	→ C ₃ H ₈	+ 1-C ₄ H ₉ •	8.0	12.9	4.0	(S1)
17	2-C ₃ H ₇ •	+ n-C ₄ H ₁₀	→ C ₃ H ₈	+ 2-C ₄ H ₉ •	8.0	12.3	4.2	(S1)
18	2-C ₄ H ₉ •	+ n-C ₄ H ₁₀	→ n-C ₄ H ₁₀	+ 1-C ₄ H ₉ •	8.0	12.9	4.0	(S1)
19	1-C ₄ H ₉ •	+ n-C ₄ H ₁₀	→ n-C ₄ H ₁₀	+ 2-C ₄ H ₉ •	8.0	10.4	4.8	(S1)
20	C ₂ H ₅ •	+ n-C ₆ H ₁₄	→ C ₂ H ₆	+ 1-C ₆ H ₁₃ •	11.5	12.3		(S2)
21	C ₂ H ₅ •	+ n-C ₆ H ₁₄	→ C ₂ H ₆	+ 2-C ₆ H ₁₃ •	11.0	10.4		(S2)
22	C ₂ H ₅ •	+ n-C ₆ H ₁₄	→ C ₂ H ₆	+ 3-C ₆ H ₁₃ •	11.0	10.4		(S2)
23	1-C ₅ H ₁₁ •	+ n-C ₆ H ₁₄	→ n-C ₅ H ₁₂	+ 1-C ₆ H ₁₃ •	11.5	12.3		(S2)
24	1-C ₅ H ₁₁ •	+ n-C ₆ H ₁₄	→ n-C ₅ H ₁₂	+ 2-C ₆ H ₁₃ •	11.0	10.4		(S2)
25	1-C ₅ H ₁₁ •	+ n-C ₆ H ₁₄	→ n-C ₅ H ₁₂	+ 3-C ₆ H ₁₃ •	11.0	10.4		(S2)
26	H•	+ n-C _m H _{2m+2}	→ H ₂	+ 1-C _m H _{2m+1} •		9-10		(S3), m ≥
27	H•	+ n-C _m H _{2m+2}	→ H ₂	+ 2-C _m H _{2m+1} •		7-8		(S3), m ≥
28	1-R•	+ n-C _m H _{2m+2}	→ RH	+ 1-C _m H _{2m+1} •		12.3		(S3), m ≥
29	1-R•	+ n-C _m H _{2m+2}	→ RH	+ 2-C _m H _{2m+1} •		10.4		(S3), m ≥
30	1-R•	+ n-C _m H _{2m+2}	→ RH	+ 3-C _m H _{2m+1} •		10.4		(S3), m ≥
31	2-R•	+ n-C _m H _{2m+2}	→ RH	+ 1-C _m H _{2m+1} •		12.9		(S3), m ≥
32	2-R•	+ n-C _m H _{2m+2}	→ RH	+ 2-C _m H _{2m+1} •		12.3		(S3), m ≥
33	H	+ 1-C ₄ H ₈	→ H ₂	+ C ₄ H ₇ •	11.0	3.9	9.8	(S1)
34	CH ₃ •	+ 1-C ₄ H ₈	→ CH ₄	+ C ₄ H ₇ •	8.0	7.3	5.7	(S1)
35	C ₂ H ₅ •	+ 1-C ₄ H ₈	→ C ₂ H ₆	+ C ₄ H ₇ •	8.0	8.3	5.4	(S1)
36	1-C ₃ H ₇ •	+ 1-C ₄ H ₈	→ C ₃ H ₈	+ C ₄ H ₇ •	8.0	8.3	5.4	(S1)
37	2-C ₃ H ₇ •	+ 1-C ₄ H ₈	→ C ₃ H ₈	+ C ₄ H ₇ •	7.6	9.7	4.6	(S1)
38	1-C ₄ H ₉ •	+ 1-C ₄ H ₈	→ n-C ₄ H ₁₀	+ C ₄ H ₇ •	8.0	8.3	5.4	(S1)
39	2-C ₄ H ₉ •	+ 1-C ₄ H ₈	→ n-C ₄ H ₁₀	+ C ₄ H ₇ •	7.6	9.7	4.6	(S1)
40	1-R•	+ 1-C _m H _{2m}	→ RH	+ C _m H _{2m-1} •		8-9		(S3), m ≥
41	2-R•	+ 1-C _m H _{2m}	→ RH	+ C _m H _{2m-1} •		9-10		(S3), m ≥
42	CH ₃ •	+ H ₂	→ CH ₄	+ H	9.6	11.3	6.1	(S1)
43	C ₂ H ₅ •	+ H ₂	→ C ₂ H ₆	+ H	9.7	15.2	5.0	(S1)
44	1-C ₃ H ₇ •	+ H ₂	→ C ₃ H ₈	+ H	9.2-9.5	15.4	4.4	(S1)
45	1-C ₄ H ₉ •	+ H ₂	→ n-C ₄ H ₁₀	+ H	9.5	15.7	4.6	(S1)
46	2-C ₄ H ₉ •	+ H ₂	→ n-C ₄ H ₁₀	+ H	9.7	17.2	4.3	(S1)
47	1-R•	+ H ₂	→ RH	+ H	9.5	15.7	4.6	(S1)
48	2-R•	+ H ₂	→ RH	+ H	9.7	17.2	4.3	(S1)
49	1-C ₅ H ₁₁ •		→ 1-C ₅ H ₁₀	+ H	13.1	38.6	1.0	(S1)
50	1-C ₅ H ₁₁ •		→ C ₂ H ₄	+ 1-C ₃ H ₇ •	13.4	28.8	4.4	(S1)
51	2-C ₅ H ₁₁ •		→ 1-C ₅ H ₁₀	+ H	13.3	40.4	0.7	(S1)

Table 3. (Continued). Arrhenius Parameters for Elementary Reactions of Some Radicals

No.	Reactant		Product	Product		log[A] ^a	E kcal/mol	log [k] ^b	Sources
	A	B		A	B				
52	2-C ₅ H ₁₁ •	→	2-C ₅ H ₁₀	H	12.7	37.9	0.8	(S1)	
53	2-C ₅ H ₁₁ •	→	C ₃ H ₆	C ₂ H ₅ •	12.7	29.1	3.6	(S1)	
54	3-C ₅ H ₁₁ •	→	2-C ₅ H ₁₀	H	13.0	37.9	1.2	(S1)	
55	3-C ₅ H ₁₁ •	→	1-C ₄ H ₈	CH ₃ •	13.7	32.7	3.5	(S1)	
56	1-C ₆ H ₁₃ •	→	C ₂ H ₄	1-C ₄ H ₉ •	12.95	28.8		(S2)	
57	2-C ₆ H ₁₃ •	→	C ₃ H ₆	1-C ₃ H ₇ •	12.42	28.3		(S2)	
58	3-C ₆ H ₁₃ •	→	1-C ₄ H ₈	C ₂ H ₅ •	14.74	29.1		(S2)	
59	3-C ₆ H ₁₃ •	→	1-C ₅ H ₁₀	C H ₃ •	14.65	32.2		(S2)	
60	1-C ₈ H ₁₇ •	→	C ₂ H ₄	1-C ₆ H ₁₃ •	13.4	28.8	4.4	(S1)	
61	2-C ₈ H ₁₇ •	→	C ₃ H ₆	1-C ₅ H ₁₁ •	13.2	28.3	4.4	(S1)	
62	3-C ₈ H ₁₇ •	→	1-C ₇ H ₁₄	CH ₃ •	13.9	33.0	3.6	(S1)	
63	3-C ₈ H ₁₇ •	→	1-C ₄ H ₈	1-C ₄ H ₉ •	12.7	29.1	3.6	(S1)	
64	1-C _m H _{2m+1} •	→	1-C _m H _{2m}	H		38-39		(C), m≥	
65	1-C _m H _{2m+1} •	→	C ₂ H ₄	1-C _n H _{2n+1} •		28-29		(C), m≥4, 2	
66	2-C _m H _{2m+1} •	→	1-C _m H _{2m}	H		38-40		(C), m≥	
67	2-C _m H _{2m+1} •	→	1-C _n H _{2n}	1-C _i H _{2i+1} •		28-29		(C), m≥4, n≥ j≥2	
68	3-C _m H _{2m+1} •	→	1-C _n H _{2n}	CH ₃ •		32-33		(C), m≥4, 2	
69	3-C _m H _{2m+1} •	→	1-C _n H _{2n}	1-C _i H _{2i+1} •		28-29		(C), m≥4, n≥ j≥2	
70	1-C ₅ H ₁₁ •	→	2-C ₅ H ₁₁ •		11.0	20	4.8	(S1)	
71	2-C ₅ H ₁₁ •	→	1-C ₅ H ₁₁ •		11.1	23.4	3.8	(S1)	
72	1-C ₆ H ₁₃ •	→	2-C ₆ H ₁₃ •		9.2	11.1, 13.7		(S2), (†)	
73	2-C ₆ H ₁₃ •	→	1-C ₆ H ₁₃ •		9.15	15.4, 14.5		(S2), (†)	
74	1-C ₇ H ₁₅ •	→	3-C ₇ H ₁₅ •		9.2	11.1	5.7	(S1)	
75	1-C ₆ H ₁₃ •	+ C ₂ H ₄	→	C ₈ H ₁₇ •	11.52	6.7		(S2)	
76	1-C ₆ H ₁₃ •	+ C ₅ H ₁₀	→	C ₁₁ H ₂₃ • (1) ^c	12.7	7.0		(S2)	
77	1-C ₆ H ₁₃ •	+ C ₅ H ₁₀	→	C ₁₁ H ₂₃ • (2)	11.82	8.7		(S2)	
78	2-C ₆ H ₁₃ •	+ C ₅ H ₁₀	→	C ₁₁ H ₂₃ • (3)	12.08	8.0		(S2)	
79	2-C ₆ H ₁₃ •	+ C ₅ H ₁₀	→	C ₁₁ H ₂₃ • (4)	11.88	9.7		(S2)	
80	C ₂ H ₅ •	+ 1-C ₃ H ₇ •	→	C ₂ H ₆	+ C ₃ H ₆	8.7	0		(S4)
81	C ₂ H ₅ •	+ 2-C ₃ H ₇ •	→	C ₂ H ₆	+ C ₃ H ₆	9.2	0		(S4)
82	H	+ 2-C ₄ H ₉ •	→	H ₂	+ 1-C ₄ H ₈	10.7	0		(S4)
83	CH ₃ •	+ 2-C ₄ H ₉ •	→	CH ₄	+ 1-C ₄ H ₈	9.0	0		(S4)
84	CH ₃ •	+ 1-C ₄ H ₇ •	→	CH ₄	+ C ₄ H ₆	9.9	0		(S4)
85	C ₂ H ₅ •	+ 1-C ₄ H ₇ •	→	C ₂ H ₆	+ C ₄ H ₆	9.1	0		(S4)
86	C ₂ H ₅ •	+ 1-C ₄ H ₇ •	→	C ₂ H ₄	+ 1-C ₄ H ₈	8.5	0		(S4)
87	H	+ 1-R•	→	RH				11.0	(S1)
88	1-R•	+ 1-R•	→	R-R				9.6	(S1)
89	1-R•	+ 2-R•	→	R-R				9.8	(S1)
90	2-R•	+ 1-R•	→	R-R				9.5	(S1)

a) The unit of preexponential factor A is 1/s for unimolecular reactions, and L/(mol · s) for bimolecular reactions.

b) The rate constant K is for radical reactions at 700 degree Kelvin. Its unit is 1/s for unimolecular reactions and in L/(mol · s) for bimolecular reactions.

c) The number of isomers.

S1) D.L. Allara and R. Shaw, J. Phys. Chem. Ref. Data, 1980, 9 (3), 523-559; and numerous references cited therein.

S2) Domine, F.; Marquaire, P.-M.; Muller, C.; Come, G.-M., Energy & Fuels, 1990, 4 (1), 2-10; and references cited therein.

S3) Generalized by the authors based on literature data.

S4) P.H. Schmicg; H.J. Ederer; K.H. Ebert, Ind. Eng. Chem. Res., 1992, 31, 29-37.

Table 4. Adsorption Properties of Activated Carbons.

Activated carbon precursor	BET N ₂ surface area, m ² /g	Macropore volume, cm ³ /g	Mesopore volume, cm ³ /g	Micropore volume, cm ³ /g
Anthracite	721	-	0.02	0.65
Grape seeds	303	0.05	0.12	0.02
Cherry stones	541	0.21	0.10	0.04
Apricot stones	750	-	0.04	0.46
Calgon	1177	0.12	0.12	0.56
Almond shells	574	0.02	0.20	0.13

Table 5. Yield of liquids and solids products and pressure build-up from thermal stressing experiments on JP8 jet fuel mixed with different activated carbons.

Sample liquid-10 ml Solid-1g	Solid on reactor walls, mg $\pm$ 10 mg	Liquid yield, ml $\pm$ 0.3 ml	Final gas pressure (cold) psi $\pm$ 100 psi	Increase of weight of solid, %
JP8+AC* from grape seeds	negligible	4.2	700	69
JP8+AC from cherry stones	negligible	4.0	800	65
JP8+AC from almond shells	negligible	3.9	500	74
JP8+AC from anthracite	0	3.5	500	49

*AC- activated carbon

Table 6. Compounds identified and weight percent of the liquids obtained after thermal stressing of A-1 alone and in the presence of the 200 mg activated carbon- PX-21.

COMPOUNDS	JETA1, WT%	JETA1+ ACTIVATED CARBON- PX-21, WT%
N-BUTANE+BUTENE	0.431	0.478
2-METHYL BUTANE	2.439	0.786
N-PENTANE+PENTENE	2.081	1.693
PENTENE	0.789	0.091
2-METHYL PENTANE	1.237	0.81
3-METHYL PENTANE	1.997	0.367
N-HEXANE+CYCLOPENTANE	2.864	2.601
HEXENE	0.384	0.059
HEXENE	0.061	0.042
METHYL-CYPENTANE+2-METHYL HEXANE	2.701	1.533
3-METHYL HEXANE	0.608	0.744
N-HEPTANE+CYCLOHEXANE	4.116	3.904
DIMETHYL CYCLOPENTANE	1.319	0.622
HEPTENE+BR ALKANE	0.119	0.098
HEPTENE/METHYL HEXENE		0.147
CYCLOHEXENE	0.512	0.171
METHYL CYCLOHEXANE	2.454	1.086
2-METHYL HEPTANE	0.818	1.11
DIMETHYL CYCLOPENTANE	0.856	0.684
BENZENE+3-METHYL HEPTANE	1.141	0.758
C2 -CYCLOHEXENE	0.146	0.105
N-OCTANE	2.722	2.179
METHYL CYCLOHEXENE	0.364	0.272
C3-CYCLOPENTANE	0.291	0.234
C3-CYCLOPENTANE	0.314	0.244
OCTENE	0.474	0.255
DIMETHYL CYCLOHEXANE	0.341	0.223
METHYL CYCLOHEXENE	0.245	0.171
DIMETHYL CYCLOHEXANE	0.515	0.22
C2-CYCLOHEXENE	0.466	0.272
TRIMETHYL CYCLOHEXANE	0.402	0.258
4-METHYL OCTANE	0.728	0.684
ETHYL CYCLOHEXANE	0.92	0.667
3-METHYL OCTANE		
TOLUENE	3.534	1.341
N-NONANE	1.348	1.404
NONENE	0.335	0.091

COMPOUNDS	JET A-1, wt %	JET A-1 + ACTIVATED CARBON PX-21, wt %
C3-CYCLOHEXANE	0.597	0.37
OCTAHYDRO PENTALENE	0.256	0.412
BR ALKANE		
C2-CYCLOHEXENE	0.314	0.101
C3- CYCLOHEXANE	0.215	0.615
C3-CYCLOHEXENE		
C4-CYCLOHEXANE	0.512	1.138
4-METHYL NONANE	0.448	0.552
ETHYL BENZENE	1.196	0.601
P-XYLENE	1.045	0.545
M-XYLENE	2.771	1.33
C4-CYCLOHEXANE	0.175	0.283
METHYL NONENE	0.355	0.576
C4-CYCLOHEXANE	0.166	0.241
C4-CYCLOHEXANE		
N-DECANE	2.134	4.584
C4-CYCLOHEXANE	0.687	0.803
DECENE	0.323	0.258
O-XYLENE	1.674	1.023
DIMETHYL NONANE	0.096	0.269
C4-CYCLOHEXANE	0.323	0.464
C3-BENZENE	0	0.45
DECENE	0.061	0.436
C5-CYCLOHEXANE	0.274	0.751
5-METHYL DECANE	0.259	0.768
4- AND 2-METHYL DECANE	0.707	2.123
N-PROPYL BENZENE	0.972	1.826
N-BUTYL CYCLOHEXANE		
C3-BENZENE (ISOMERS)	3.155	1.337
C3-BENZENE	0.873	0.601
C3-BENZENE		
N-UNDECANE	3.234	7.741
C3-BENZENE	3.094	2.65
DECALIN	0.702	1.198
DIMETHYL NONANE	0	0.496
C5-CYCLOHEXANE	0.204	0
C4-BENZENE	1.01	0.943
C3-BENZENE	1.496	1.421
BR ALKANE	0.207	0.513

COMPOUNDS	JET A-1, wt %	JET A-1 + ACTIVATED CARBON- PX-21, wt %
C4-BENZENE	0.256	0.793
	0	1.432
C4-BENZENE	1.036	1.564
C4-BENZENE	1.426	0
N-BU BENZENE+ N-C5 CYCLOHEXANE	0.515	1.543
C4-BENZENE	0.309	0.248
C4-BENZENE	1.278	1.163
DECALIN	0.291	0.391
INDAN+C4-BENZENE	0.899	1.051
C1-DECALIN	0.378	0.45
C4-BENZENE	0.8	0.688
C4-BENZENE	0.186	0.681
N-DODECANE	2.078	4.693
C4-BENZENE	1.1	1.449
C4-BENZENE	0.148	0.457
C5-BENZENE		
C5-BENZENE (ISOMERS)+ METHYL INDAN	0.297	0.346
C4-BENZENE	0.119	0.182
C5-BENZENE+METHYL INDAN	0.966	0.583
C2-DECALIN+METHYL INDAN	0.262	0.482
C4-BENZENE	0.748	0.922
C4-BENZENE	1.057	1.425
C5-BENZENE	0	0.101
BR ALKANE	0	0.405
C5-BENZENE+C2-INDAN	0.341	0.632
C5-BENZENE (ISOMERS)	0.536	0.51
C5-BENZENE	0.218	0.667
C5-BENZENE	0.076	0.262
N-PENTYL BENZENE	0.015	0.293
N-HEXYL CYCLOHEXANE		
C5-BENZENE	0.143	0.332
C5-BENZENE	0.172	0.258
C5-BENZENE	0.14	0.258
C5-BENZENE	0.148	0.416
METHYL INDAN	0.259	0.391
C4-BENZENE	1.29	1.407
C5-BENZENE	0.239	0

COMPOUNDS	JET A-1, wt%	JET A-1+ ACTIVATED CARBON PX-21, wt%
C5-BENZENE	0.265	0
N-TRIDECANE+C5-BENZENE	0.125	1.023
METHYL INDAN+C6-BENZENE	0.498	0.646
C5-BENZENE	0.076	0
C5-BENZENE	0.064	0
C6-BENZENE+C2-INDAN	0.064	0
C5-BENZENE+METHYL INDENE	0.271	0.213
C2-INDAN+C5-BENZENE	0.405	0.391
C2-INDAN		
C3-INDAN+C5-BENZENE	0.346	0.513
C6-BENZENE	0.148	0.269
C2-INDAN+C6-BENZENE	0.76	0.391
C5-BENZENE	0.14	0.241
C5-BENZENE+C6-BENZENE	0.227	0.251
NAPHTHALENE	1.764	1.442
N-TETRADECANE	0	0.168
C6-BENZENE	0.227	0
C2-INDAN	0.052	0.035
C2-INDAN	0.128	0.136
C3-INDAN+C2-INDENE	0.245	0.119
C2-INDENE	0.079	0.105
C3-INDAN	0.189	0.108
C2-INDAN+C2-INDENE	0.116	0.105
C6-BENZENE+C3-INDAN	0.114	0.031
2-METHYL NAPHTHALENE	1.423	1.142
1-METHYL NAPHTHALENE	0.969	0.817
2-ETHYL NAPHTHALENE	0.253	0.129
DIMETHYL NAPHTHALENE	0.23	0.209
DIMETHYL NAPHTHALENE	0.18	0.126
1-ETHYL NAPHTHALENE	0.105	0.08
DIMETHYL NAPHTHALENE	0.236	0.157
DIMETHYL NAPHTHALENE	0.509	0.328
C3-NAPHTHALENE	0.049	0.045
DIMETHYL NAPHTHALENE (ISOMERS)	0.073	0.045
DIMETHYL NAPHTHALENE (ISOMERS)	0.049	0.063
DIMETHYL NAPHTHALENE	0.073	0.059
DIMETHYL NAPHTHALENE	0.096	0.014

COMPOUNDS	JET A-1, wt%	JET A-1+ ACTIVATED CARBON PX-21, wt %
DIMETHYL NAPHTHALENE	0.073	0.042
C3-NAPHTHALENE	0.02	0.059
DIMETHYLNAPHTHALENE	0.082	0.042
C3-NAPHTHALENE	0.093	0.073
C3-NAPHTHALENE (ISOMERS)	0.052	0.059
C3-NAPHTHALENE (ISOMERS)	0.058	0.024
C3-NAPHTHALENE (ISOMERS)	0.116	0
C3-NAPHTHALENE (ISOMERS)	0.07	0
C3-NAPHTHALENE	0.105	0
C3-NAPHTHALENE	0.029	0
C3-NAPHTHALENES	0.087	0
C3 AND C4-NAPHTHALENES	0.032	0
C3 AND C4 NAPHTHALENES	0.044	0
FLUORENE+C4-NAPHTHALENE	0.084	0
METHYLFLUORENE+ C4-NAPHTHALENE	0.125	0
METHYLFLUORENE	0.087	0
C2-FLUORENE	0.093	0
C2-FLUORENE	0.02	0
C2-FLUORENE	0.099	0
C2-FLUORENE	0.047	0
METHYLFLUORENE	0.076	0
C2-FLUORENE	0.044	0
C2-FLUORENE	0.044	0
C2-FLUORENE		0
C2-FLUORENE	0.55	0
PHENANTHRENE	0.09	0
ANTHRACENE	0.049	0
METHYLPHENANTHRENE	0.044	0
METHYLPHENANTHRENE	0.032	0
METHYLPHENANTHRENE	0.015	0
METHYLPHENANTHRENE	0.026	0
PYRENE	0.079	0
METHYLPYRENE	0.044	0
METHYLPYRENE	0.032	0
METHYLPYRENE	0.035	0

Table 7. Effects of Tetralin (THN) on the Pyrolysis of n-Tetradecane at 450 °C

Reactor Residence Time in Sandbath Preheated to 450°C ^a											
	6 min	6 min	12 min	12 min	21 min	21 min	30 min	30 min	240 min	240 min	240 min
ID No.	TS84	MTS32	TS83	MTS31	TS82	MTS30	TS85/86	MTS26	TS67	MTS20	MTS21
With H-donor	No	10% THN	No	10% THN	No	10% THN	No	10% THN	No	10% THN	25 % THN
Conversion (mol %) ^b	3.98	2.64	16.92	5.39	31.68	10.84	53.33	33.76	97.08	95.48	91.98
Yields (mol %) ^b											
Hydrogen (H ₂)							1.17		8.09		
Methane (C ₁)	0.45	0.38	1.73	0.59	3.90	0.98	8.33	2.39	70.31	45.85	28.06
Ethane (C ₂)	1.04	1.01	3.53	1.43	6.78	2.21	13.76	4.55	74.48	56.05	37.40
Ethylene	0.37	0.22	1.06	0.40	1.62	0.55	2.21	0.76	2.38	1.41	1.11
Propane (C ₃)	0.83	0.60	1.95	0.78	3.58	1.22	7.08	2.51	46.93	38.24	26.86
Propylene	0.49	0.41	1.57	0.64	2.70	1.07	5.20	2.08	10.52	6.40	8.21
iso-Butane	0	0.02	0		0		0.03		1.45	0.92	0.42
n-Butane (n-C ₄)	0.35	0.31	2.02	0.49	4.31	1.31	8.41	5.26	17.62	24.22	20.5
1-Butene	0.39	0.34	1.73	0.63	3.63	1.27	6.74	3.55	2.83	2.97	3.37
Pentane (n-C ₅)	0.16	0.13	1.17	0.35	3.15	0.73	7.00	5.48	14.71	17.70	20.06
1-Pentene	0.41	0.28	2.13	0.69	3.36	1.28	5.71	4.99	2.45	1.27	5.02
n-Hexane (n-C ₆)	0.23	0.18	1.21	0.43	2.75	0.84	5.67	4.82	12.65	14.36	18.09
1-Hexene	0.40	0.25	2.10	0.60	3.20	1.16	4.96	3.76	2.70	1.36	1.59
n-Heptane (n-C ₇)	0.24	0.20	1.28	0.44	2.70	0.93	5.15	2.27	9.21	10.62	9.51
1-Heptene	0.35	0.22	1.61	0.50	2.50	1.01	3.35	3.34	2.36	2.03	3.00
n-Octane (n-C ₈)	0.21	0.18	1.13	0.39	2.36	0.83	4.44	2.66	6.99	7.95	7.05
1-Octene	0.31	0.22	1.36	0.47	1.95	0.90	2.61	2.24	0.06		
n-Nonane (n-C ₉)	0.21	0.16	1.04	0.37	2.11	0.80	3.66	2.40	4.93	5.21	5.28
1-Nonene	0.31	0.21	1.23	0.44	1.77	0.85	2.31	1.73	0.09	0.14	0.17
n-Decane (n-C ₁₀)	0.19	0.15	0.92	0.34	1.82	0.73	2.94	2.05	3.25	3.70	3.90
1-Decene	0.29	0.21	1.13	0.43	1.53	0.80	1.47	1.46	0.03		
n-Undecane (n-C ₁₁)	0.20	0.16	0.93	0.35	1.76	0.75	2.69	1.96	2.30	2.72	3.05
1-Undecene	0.27	0.19	1.00	0.39	1.32	0.72	1.27	1.23			
n-Dodecane (n-C ₁₂)	0.03	0.02	0.19	0.04	0.45	0.13	0.82	0.44	0.81	0.85	0.89
1-Dodecene	0.27	0.18	0.97	0.37	1.28	0.70	1.17	1.15			
n-Tridecane (n-C ₁₃)	0.02	0	0.09	0.01	0.26	0.05	0.51	0.21	0.40	0.40	0.38
1-Tridecene	0.06	0.05	0.22	0.10	0.32	0.17	0.25	0.26			
n-Tetradecane (n-C ₁₄)	96.02	97.36	83.08	94.61	68.32	89.16	46.67	66.24	2.92	4.52	8.02
1-Tetradecene			0.02		0.14		0.21				
n-Pentadecane (n-C ₁₅)	0.08	0.09	0.14	0.09	0.24	0.10	0.36	0.18		0.05	0.15
n-Hexadecane (n-C ₁₆)			0.06		0.16	0.02	0.26	0.09	0.06	0.22	0.02
n-Heptadecane (n-C ₁₇)			0.04		0.11		0.17	0.08		0.02	0.04
n-Octadecane (n-C ₁₈)	0.13	0.13	0.13	0.13	0.15	0.13	0.18	0.13		0.03	
n-Nonadecane (n-C ₁₉)			0.02		0.07		0.09	0.05			
n-Eicosane (n-C ₂₀)			0.02		0.06		0.07	0.06			
n-Heneicosane (n-C ₂₁)			0.02		0.04		0.05	0.03			
n-Docosane (n-C ₂₂)			0.01		0.03		0.04	0.02			
n-Tricosane (n-C ₂₃)			0.01		0.02		0.03	0.02			
Alkylcyclopentanes			0.06		0.20		0.69	0.24	3.52	3.52	5.22
Alkylcyclohexanes			0.13		0.57		1.71	0.49	5.62	5.99	4.44
Alkylbenzenes							0.44	0.29	21.39	13.19	6.59
Tetralin ^c		94.83		94.80		93.48		83.03		3.95	22.47
1-Methylindane ^c		0.09		0.16		0.34		4.10	0.36 ^d	6.48	12.06
Naphthalene ^c		0.68		0.83		1.36		7.29	0.58 ^d	101.85	61.67
Other Polyaromatics									0.24	0.91	0.94
Solids (wt% of C ₁₄)									3.0	0.7	0.2

a) Pyrolysis of 5 mL sample of n-C₁₄ and C₁₄-tetralin (THN) in 25 mL reactor under 0.69 MPa UHP N₂ (cold).

b, d) Molar percentage based on the initial molar number of n-tetradecane feed, unless otherwise mentioned.

c) Yield in molar percentage based on the initially added amount of H-donor tetralin.

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

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

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

Table 9. Products from Pyrolysis of Tetralin at 450 °C under UHP N₂.

Residence time	None	30 min	60 min	150 min	240 min	480 min
ID No.	Orig. Feed	TS79	TS36	TS56	TS6	TS69
<u>Conversion (mol%)</u>	3.27	5.42	6.88	13.73	19.92	35.62
<u>Yield (mol %)</u>						
H ₂		0.73	2.37	3.55	3.73	9.39
Methane		0.01	0.12	0.23	0.41	1.96
Ethane		0.07	0.09	0.18	0.21	0.88
Ethylene			0.01	0.06	0.01	0.04
Propane		0.02	0.04	0.16	0.27	0.32
Propylene		0.04	0.02	0.09	0.06	0.18
n-Butane		0.02	0.01	0.13	0.23	0.14
1-Butene				0.05	0.03	0.01
Toluene		0.03	0.03	0.13	0.13	0.56
Ethylbenzene	0.05	0.07	0.05	0.11	0.16	0.49
o-Xylene					0.02	0.05
n-Propylbenzene		0.11	0.11	0.08	0.10	0.12
2-Ethyltoluene			0.03	0.01	0.02	0.05
trans-Decalin	0.11	0.12	0.18	0.37	0.20	0.30
n-Butylbenzene		0.19	0.22	0.55	0.48	1.01
cis-Decalin	0.25	0.23	0.17	0.17	0.11	0.08
2-Methylindane		0.06	0.10	0.23	0.47	0.71
1-Methylindane	0.08	1.81	2.87	6.11	12.68	20.71
Tetralin (THN) ^a	96.73	94.58	93.12	86.57	80.08	64.38
1,2-DHNa	0.65	0.12	0.12	0.15	0.12	0.14
Naphthalene	0.31	1.56	1.63	3.24	3.98	8.83
α-Tetralol ^b	0.57	0.05				
α-Tetralone ^c	1.18	0.79	0.74	0.52	0.22	0.07

a) 1,2-Dihydronaphthalene (DHN), and 1,2,3,4-tetrahydronaphthalene (THN).

b) 1,2,3,4-tetrahydro-1-naphthol.

c) 3,4-dihydro-1-naphthalenone

Table 10. Proximate analysis (as rec'd) of DECS-6 and DECS-16 (from Penn State Coal Data Base)

Coal	%Moisture	%Ash	%Volatile	%Fixed carbon
DECS-6	4.73	5.56	42.40	47.31
DECS-16	5.20	13.17	39.23	42.40

Table 11. Ultimate analysis (dmmf) and rank of DECS-6 and DECS-16 (from Penn State Coal Data Base)

Coal	Rank	% C	% H	% N	% O
DECS-6	HVAb	81.87	6.29	1.56	10.27
DECS-16	HVA/Bb	82.35	5.97	1.51	10.17

Table 12. Relaxation parameters for the aromatic carbons of DECS-6 and DECS-16

Coal	T ^{CH} (ms)	T _H ^{1p} (ms)	T ^{1H} (ms)	T _{2a} (us)	T _{2b} (us)
DECS-6	0.196	5.127	33.34	22.4	290.0
DECS-16	0.398	5.824	29.12	18.6	239.5

Table 13. Relaxation parameters for the aliphatic carbons of DECS-6 and DECS-16

Coal	T ^{CH} (ms)	T _H ^{1p} (ms)	T ^{1H} (ms)	T _{2a} (us)	T _{2b} (us)
DECS-6	0.609	5.10	52.97	21.8	62.5
DECS-16	0.802	8.768	48.32	34.5	78.74

Table 14. Some Important Chemical Structural Parameters of the Blind Canyon Coals

Coal	DECS-6	DECS-16
Carbon aromaticity	0.68	0.65
Aromatic +Carbonyl +Carboxyl /Total carbons	0.70	0.69
Aliphatic /Total carbons	0.30	0.31
Hydrogen aromaticity	0.21	0.17
Protonated aromatic carbons/Aromatic carbons	0.29	0.23
Nonprotonated aromatic/Aromatic carbons	0.71	0.77
Phenolics/Aromatic carbons	0.11	0.16
Alkylated aromatic/Aromatic carbons	0.29	0.32
Bridgehead aromatic/Aromatic carbons	0.31	0.29
Methylated aliphatic carbons/Aliphatic carbons	0.15	0.31
Nonmethylated aliphatic /Aliphatic carbons	0.85	0.69
Carboxyl /Total carbons	0.03	0.01
Carbonyl/Total carbons	0.02	0.02
Phenolics/Total carbons	0.07	0.10
Oxygenated aliphatic carbons/Total carbons	0.03	0.02
Oxygenated carbons/Total carbons	0.15	0.15

Table 15. Catalytic Liquefaction of DECS-9 Subbituminous Coal

Catalyst precursor	Solvent for catalyst loading ^a	In-situ pretreat at LT ^b	Reaction temp, °C	Oil + Gas dmmf wt%	Asphaltene dmmf wt%	Preasph. dmmf wt%	Conversion dmmf wt%
None	None	No	400	16.0	9.4	6.8	32.2
MoCo-TC1	CH ₃ CN	No	400	22.8	4.8	5.2	32.8
MoCo-TC1	THF	No	400	18.7	12.8	14.8	46.3
MoCo-TC2	Toluene	No	400	32.4	18.0	24.2	74.6
MoCo-TC2	THF	No	400	25.8	17.9	23.7	67.4
MoCo-TC3	Toluene	Yes	400	33.8	17.8	19.9	71.5
MoCo-S ^c	CHCl ₃	No	400	21.3	12.6	16.0	49.8
MoCo-S ^d	CH ₂ Cl ₂	No	400	25.2	16.0	27.1	68.3
Mo(CO) ₆	1-MN	No	400	25.2	10.6	16.5	52.3
Co ₂ (CO) ₈	1-MN	No	400	23.7	12.6	15.0	51.3
Mo(CO) ₆ + Co ₂ (CO) ₈	1-MN	No	400	23.9	18.9	17.8	60.6
None	None	Yes	400	18.9	8.2	7.0	34.1
MoCo-TC2	Toluene	Yes	400	37.0	19.8	22.0	78.7
MoCo-TC2	Toluene	Yes	425	46.7	19.5	15.0	81.1
MoCo-TC3	Toluene	Yes	425	46.3	17.5	12.9	76.6
Mo(CO) ₆	1-MN	Yes	400	24.2	11.8	16.4	52.4
Co ₂ (CO) ₈	1-MN	Yes	400	23.6	12.4	14.2	50.2

a) The impregnating solvent was removed by evaporation in vacuum before the reaction solvent 1-MN was added.

b) In-situ low-temperature pretreatment at 200°C for 15 min followed by heat-up to reaction temperature.

c) Used shortly after synthesis without further purification. Decomposition during storage was noticed.

d) Used after further purification immediately before use. The purified MoCo-S was impregnated on to coal using excess amount of CH₂Cl₂ solution.

APPENDIX 2
REACTION SCHEMES

Initiation **Propagation** **Termination**

Scheme I. General mechanisms of pyrolysis of long-chain n-alkanes C_mH_{2m+2} at elevated pressures at 400-450°C Modified from C. Song, W.-C. Lai, and H.H. Schobert, Am. Chem. Soc. Div. Fuel Chem. Prepr., 1992, 37 (4), 165: 1663]. The reaction shown by eq. 8 also applies to the primary radicals with ≥ 5 carbon atoms produced from β -scissic reactions (eqs. 4 and 5).

Scheme II. Different reaction pathways for the formation of n-dodecane (eq. 4-I) and 1-dodecene (eqs. 5-I and 6-I) during pyrolysis of n-tetradecane.

Scheme III. Possible 1,5-shift (top) and 1,4-shift (bottom) isomerization of primary $C_jH_{2j+1}\bullet$ radicals followed by β -scission. Such radicals include both $\text{pri-}C_mH_{2m+1}\bullet$ and $\text{pri-}C_mH_{2(m-n)+1}\bullet$ radicals shown in Scheme I.

Scheme IV. Hydrogenation of 1-alkene products during long-duration pyrolysis which is accompanied by the cyclization and dehydrogenation reactions to generate H_2 .

Scheme V. Ring-closure reaction through the cyclization of 5-hexenyl radical.

Scheme VI. H-abstraction from tetralin by primary (k_1) and secondary radicals (k_2).

Scheme VII. Inhibition of decomposition of long-chain paraffins by interrupting the radical chain reaction by hydrogen-donor molecules.

Scheme VIII. Radical stabilization via hydrogen transfer from tetralin and decalin.

Pure	450°C/30 min	1.7	1.3	0.2 mol%
		12.7	4.0	0.5 mol%
With C14 or n-BB	450°C/30 min	5.9	4.5	mol%
		90.9	5.7	mol%
10% Tetralin-C14	450°C/30 min	27.1	3.6	mol%
		97.0	2.3	mol%
10% Tetralin-BB	450°C/30 min	64.1	12.6	mol%
		92.3	5.6	mol%
25% Tetralin-C14	450°C/30 min			
25% Tetralin-BB	450°C/30 min			

Scheme IX. Products from tetralin for pyrolysis of itself and its mixture with n-C14 or n-BB.

Scheme X. Isomerization of tetralin to 1-methylindan and the dehydrogenation of 2-tetralyl radical in the presence of reactive compounds.

APPENDIX 3
FIGURES

Figure 1. The Disappearance of Octylbenzene (mol%) with Stressing Time under 400, 425 and 450°C.

Figure 2. Relationship of Gas Yield with Reaction Time and Temperature.

Figure 3. Relationship of Solid Yield with Reaction Time and Temperature.

Figure 4. Relationship of Liquid Yield with Reaction Time and Temperature.

Figure 5. Reaction Kinetics of Octylbenzene in the Temperature range between 400 and 450°C.

Figure 6. The Arrhenius Plot for the Pyrolysis of Octylbenzene.

Figure 7. The T-P profile of the 25 mL microreactor showing the increase in temperature (left axis) and pressure (right axis) inside the reactor containing 5 mL n-C14 under initial N₂ pressure (cold) of 0.69 MPa (100 psi) during and after the heat-up.

Figure 8. Relationship between tetradecane conversion and system pressure during pyrolysis at 450°C for 6-240 min under initial N₂ pressure of 0.69 MPa.

Figure 9. Expanded retention time windows (1.5-3.9 min; 4-23 min) of capillary gas chromatograms of liquid products from $n\text{-C}_{14}$ pyrolysis in sandbath of 450°C for 6 (A), 12 (B), 21 (C) and 30 min (D).

Figure 10. Carbon number distribution of paraffinic (left) and olefinic (right) products from pyrolysis of n-tetradecane at 450°C under initial N₂ pressure of 0.69 MPa (100 psi).

Figure 11. Retention time window (20-50 min) of GC-MS total ion chromatogram of liquids from n-C₁₄ pyrolysis at 450°C for 30 min.

Figure 12. Temporal plots of olefinic and paraffinic products from $n\text{-C}_{14}$ at 450°C .

Figure 13. Compound class distribution of products from $n\text{-C}_{14}$ pyrolysis.

Figure 14. PLM micrographs of solid deposits collected from the top (a), and bottom (b) reactor walls after thermal stressing of Jet A at 450 °C for 5 hours with 8 nickel grids at the bottom of the reactor.

Figure 15. PLM micrographs of Ni grid-deposit interface showing the incorporation of Ni particles into the carbon deposit after thermal stressing of Jet A at 450 °C for 3 hours (a) top Ni grid, and (b) bottom Ni grid.

Figure 16. SEM micrographs showing the crystallite layer on metal grids after thermal stressing with Jet A at 450 °C on top Ni grid for 1 hour (a), on top SS grid for 1 hour (b).

Figure 17. SEM micrographs of carbon deposits formed from thermal stressing of Jet A at 450 °C for 3 hours on bottom metal grids: (a) on Ni, (b) on Cu, and (c) on SS.

Figure 18. PLM micrographs of reactor deposits obtained from dodecane at 450 °C for 5 hours with nickel grids at the bottom, showing the incorporation of liquid-like spherules into the deposit layer on the top wall (a) and preferred growth of coarser structures from a fluid-phase on deposits from bottom walls.

Figure 19. SEM micrographs of deposits on SS grids showing the different effects of surface roughness. Deposits were generated from n-dodecane at 450 °C for 3 hours on top SS grid (a), and on bottom SS grid (b).

Figure 20. Measurements of solid particle and deposit formation in mixtures of JP-8C and tetradecane after 6 hours at 450°C under nitrogen: a. Mass of all solid material as a fraction of the initial mass of material charged to the reactor. b. Mass of particles, separated from the liquid products by filtration, divided by the total volume of the reactor. c. Mass of deposit removed from the vertical walls of the tube, divided by the area of the vertical walls. d. Mass of deposit on the bottom of the reactor, divided by the plan area of the reactor.

200 μ m

Position A

400 μ m

Position B

Figure 21. Polarized-Light Micrographs of Activated Carbon from Grape Seeds after Thermal Stressing with JP8 Jet Fuel.

100 μ m

Position A

100 μ m

Position B

Figure 22. Polarized-Light Micrographs of Activated Carbon from Cherry Stones after Thermal Stressing with JP8 Jet Fuel.

100 μ m

Position A

400 μ m

Position B

Figure 23. Polarized-Light Micrographs of Activated Carbon from Almond Shells after Thermal Stressing with JP8 Jet Fuel.

800 μ m

Position A

800 μ m

Position B

Figure 24. Polarized-Light Micrographs of Activated Carbon from Anthracite with Thermal Stressing with JP8 Jet Fuel.

40 μ m

Position A

200 μ m

Position B

Figure 25. Polarized-Light Micrographs of Activated Carbon from Apricot Stones (Position A) and Commercial Activated Carbon Calgon (Position B) after Thermal Stressing with JPTS Jet Fuel.

400 μ m

Position A

400 μ m

Position B

Figure 26. Polarized-Light Micrographs of Powdered Activated Carbon from Apricot Stones after Thermal Stressing with JPTS Jet Fuel.

200 μ m

Position A

400 μ m

Position B

Figure 27. Polarized-Light Micrographs of Solid Deposit Obtained after Thermal Stressing of A-1 Jet Fuel at 450°C.

100 μ m

Position A

200 μ m

Position B

Figure 28. Polarized-Light Micrographs of Solid Deposit Obtained after Thermal Stressing of JPTS Jet Fuel at 450°C.

A-1+PX-21, 200mg
450°C, 5hours

A-1

Figure 29. Liquid Products from Thermal Stressing of A-1 Jet Fuel with and without PX-21 Activated Carbon.

JPTS+PX-21, 100mg JPTS
450°C, 5 hours

Figure 30. Liquid Products from Thermal Stressing of JPTS Jet Fuel with and without PX-21 Activated Carbon.

Figure 31. Percent Weight Plotted versus Alkane Carbon Numbers for the Stressed Products.

Figure 32. Percent Weight Plotted versus Number of Alkyl Groups on Benzene for the Stressed Products.

Figure 33. Percent Weight Plotted versus Number of Alkyl Groups on Naphthalenes from the Stressed Products.

Figure 34. Percent Weight of Alkanes from A-1 Jet Fuel Stressed Alone Plotted versus Percent Weight of Alkanes from A-1 Jet Fuel Stressed with Activated Carbon PX-21.

Figure 35. Percent Weight of Alkenes from A-1 Jet Fuel Stressed Alone Plotted versus Percent Weight of Alkenes from A-1 Jet Fuel Stressed with Activated Carbon PX-21.

Figure 36. Percent Weight of Cycloalkanes from A-1 Jet Fuel Stressed Alone Plotted versus Percent Weight of Cycloalkanes from A-1 Jet Fuel Stressed with Activated Carbon PX-21.

Figure 37. Percent Weight of Alkylbenzenes from A-1 Jet Fuel Stressed Alone Plotted versus Percent Weight of Alkylbenzenes from A-1 Jet Fuel Stressed with Activated Carbon PX-21.

Figure 38. Percent Weight of Naphthalenes from A-1 Jet Fuel Stressed Alone Plotted versus Percent Weight of Naphthalenes from A-1 Jet Fuel Stressed with Activated Carbon PX-21.

100 μ m

Position A

200 μ m

Position B

Figure 39. Polarized-Light Micrographs of Activated Carbon PX-21 after Thermal Stressing with A-1 Jet Fuel.

80 μ m

Position A

400 μ m

Position B

Figure 40. Polarized-Light Micrographs of Activated Carbon PX-21 after Thermal Stressing with JPTS Jet Fuel.

Dodecane at 425°C under 100 psi air

Figure 41. Infrared Spectra of Dodecane samples stressed under 100 psi air at 425°C for 0, 1, 3, 6, 12, and 18 h.

Figure 42. Infrared Spectra of Dodecane + 5% Benzyl Alcohol Samples Stressed Under 100 psi Air at 425°C for 1, 3, 6, 9, 12 and 18 h.

Figure 43. A Plot of Absorbance of Infrared Band at 1642 cm⁻¹ vs Time of Stressing for (top) Dodecane Samples Stressed Under 100 psi Air at 425°C and (bottom) for Samples of Dodecane + 5% Benzyl Alcohol Stressed Under 100 psi Air.

Figure 44. Scale Expanded ^1H NMR Spectra in the Olefinic Region of Pure Dodecane Thermally Stressed for the Times Indicated over Air at 425°C .

Figure 45. Scale Expanded ^1H NMR Spectra in the Olefinic Region of Dodecane Containing 5% wt Benzyl Alcohol Thermally Stressed for Times Indicated Over Air at 425°C .

Figure 46. A Plot of the Amount of Dodecane Present vs Time of Stressing (top) for Pure Dodecane and Dodecane + 5% Benzyl Alcohol Samples Stressed Under 100 psi Air at 425°C and (bottom) for Pure Dodecane and Dodecane + 5% Benzyl Alcohol Samples Stressed Under 100 psi Nitrogen at 425°C.

Figure 47. Gas Chromatogram of Dodecane + 5% Benzyl Alcohol Sample Stressed for 3 h at 425°C Under 100 psi Air Showing Degradation Products of Benzyl Alcohol.

Figure 48. System pressure change during pyrolysis of n-tetradecane, tetralin and their mixture (10 vol% tetralin - 90 vol% n-tetradecane) under initial (cold) N₂ pressure of 0.69 MPa (100 psi).

Figure 49. Inhibiting effect of tetralin (10 vol%) on decomposition of n-tetradecane during its pyrolysis at 450°C.

Figure 50. Effects of adding tetralin (10 vol%) on the molar ratio of 1-alkene to the corresponding n-alkane.

Figure 51. Effects of addition tetralin on the early stage of n-tetradecane pyrolysis at 450°C (nominal residence time = 6 min; real RT at 450°C $\leq$ 3 min). The molar yields of n-alkanes and 1-alkenes are based on n-tetradecane.

Figure 52. Effects of adding tetralin on the molar yields of n-alkanes and 1-alkenes from tetradecane after RT of 21 min (real RT at 450°C $\leq$ 18 min).

Figure 53. Effects of adding tetralin on the molar yields of n-alkanes and 1-alkenes from tetradecane after RT of 30 min (real RT at 450°C $\leq$ 27 min).

Figure 54. Effects of adding tetralin on the molar yields of n-alkanes and 1-alkenes for long-duration pyrolysis of tetradecane (RT = 1 h).

Figure 55. Carbon number distribution of n-alkanes produced from pyrolysis of n-C₁₄ alone.

Figure 56. Effect of tetralin addition on the formation of solid deposits from n-tetradecane (left), a petroleum-derived JP-8 jet fuel (middle) and n-butylbenzene (right) at 450 °C for 4 h under initial N₂ pressure of 0.69 MPa (100 psi).

Figure 57. Product distribution from pyrolysis of tetralin (THN) alone at 450°C under 0.69 MPa UHP N₂.

Figure 58. Variation of aromatic carbon intensity for DECS-6 with contact time. A curve simulation is also shown.

Figure 59. Variation of aliphatic carbon intensity for DECS-6 with contact time. A curve simulation is also shown.

Figure 60. Variation of aromatic carbon intensity for DECS-6 with inversion recovery time. A curve simulation is also shown.

Figure 61. Variation of aliphatic carbon intensity for DECS-6 with inversion recovery time. A curve simulation is also shown.

Figure 62. (a) CPMAS spectrum of DECS-6. $CT = 1$ ms, pulse delay = 1 s and 18404 acquisition scans. (b) Bloch decay spectrum of DECS-6. Pulse delay = 80 s and 4127 acquisition scans.

Figure 63. An experimental spectrum of DECS-6 by Bloch decay and its simulation spectrum by LAB. CALC..

Figure 64. Variation of aromatic carbon area for DECS-6 with dephasing time.

Figure 65. Variation of aliphatic carbon area for DECS-6 with dephasing time.

Figure 66. Plot to show product distribution vs temperature--no catalyst.

Figure 67. Plot t show product distribution vs time--no catalyst.

Figure 68. Dehydrogenation reaction pathway of abietic acid in rosin.

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OTHER ALKYL BENZENES & SUBSTITUTED NAPHTHALENES

Figure 69. Cracking reaction pathway of rosin.

Figure 70. Plot to show product distribution vs time--NiMo catalyst.

Figure 71. Histogram to product distribution with various catalysts.

Figure 72. Plot to show detailed relationship between major mono- and bicyclics.

Figure 73. Plot to show product distribution vs time--Ni-Y catalysts.

Figure 74. Plot to show detailed relation between major mono- and bicyclics-Ni-Y catalysts.

Figure 75. Plot to show ratio of 3-ring/1+2 ring compounds--various catalysts.

Figure 76. Structure of the three different bimetallic thio cubane clusters [MoCo-TC1: $\text{Mo}_2\text{Co}_2\text{S}_4(\text{S}_2\text{CNEt}_2)_2(\text{CH}_3\text{CN})_2(\text{CO})_2$; MoCo-TC2: $\text{Mo}_2\text{Co}_2\text{S}_4\text{Cp}_2(\text{CO})_2$; MoCo-TC3: $\text{Mo}_2\text{Co}_2\text{S}_4(\text{CP}^*)_2(\text{CO})_2$].

Figure 77. Structure of the bimetallic sulfide complex $(\text{Co}(\text{MoS}_4)_2)^{3-}$ [cobalt bis(tetrathiomolybdate) trianion].

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