1961 1 3 1962

Technical Progress Report

February 1993 – March 1993

FILE: Songs; SY: H; G: Song; PG: Hitches; B: M; W: 1; M: M; C: 1

Contributions from

R. A. Anderson, E. B. Anderson, D. Clifford, J.-L. Fauriol, K. Gargava, L. Han, W.-C. Tsai,
J. Li, P. Parfenov, R. Samhanic, L. Selvaraj, E. Yeom

July 1993

Prepared for U.S. Department of Energy
under
Contract No. DE-FG22-92PC92104

ADVANCED THERMALLY STABLE JET FUELS

Technical Progress Report February 1993 - March 1993

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

Contributions from:

R. Arumugam, J. Bortiatynski, D. Clifford, J.-L. Faulon, K. Gergova, L. Hou, W-C. Lai,
J. Li, D. Parfitt, P. Sanghani, L. Selvaraj, E. Yoon

DISCLAIMER

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

July 1993

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

OBJECTIVES.....	1
SUMMARY.....	1
TECHNICAL PROGRESS.....	4
Task 1. Investigation of the Quantitative Degradation Chemistry of Fuels.....	5
Condensed-Phase Pyrolysis of Long-Chain Paraffins. Unusual Effects of Sample Volume and Inert Gas Pressure (Contributed by Wei-Chuan Lai and Chunshan Song)	4
Task 2. Investigation of Incipient Deposition.....	9
Growth and Deposition of Particles During Heating of Coal-Derived Aviation Gas Turbine Fuels (Contributed by Prashant Sanghani and Peter M. Walsh)	9
Task 3. Characterization of Solid Gums, Sediments, and Carbonaceous Deposits.....	10
1. Effects of Adding Solid Carbons on Thermal Degradation of Jet Fuel (Contributed by Katia Gergova, Rathnamala Arumugam, and Semih Eser)	10
2. Surface Effects on the Formation of Carbon Deposits—A Literature Review (Contributed by Jun Li)	15
Task 4. Coal-based Fuel Stabilization Studies.....	36
1. Thermal Stability Studies Using the Model Compound Dodecane (Contributed by Leena Selvaraj, Michael M. Coleman and Chunshan Song)	36
2. Screening Potential Jet Fuel Stabilizers Using the Model Compound Dodecane (Contributed by Emily M. Yoon, Michael M. Coleman and Chunshan Song)	44
Task 5 Exploratory Studies on the Direct Conversion of Coal to High Quality Jet Fuels.....	50
1 Characterization of Isolated Resinite Maceral (Contributed by David J. Clifford, Lei Hou, Jacqueline Bortiatynski and Patrick G. Hatcher)	46
2. Statistical Models for Bituminous Coal: A Three-Dimensional Evaluation of Structural and Physical Properties based on Computer-generated Structures (Contributed by Jean-Loup Faulon and P.G. Hatcher)	50
3. Novel Bimetallic Dispersed Catalysts from Heteronuclear Organometallic Clusters for Promoting Coal Liquefaction (Contributed by Derrick Parfitt and Chunshan Song)	61
Appendix 1. Tables.....	67
Appendix 2. Figures.....	76

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

This project was initiated on August 1, 1992. The starting date resulted in this project being one month out of synchronization with the normal quarterly calendar (i.e., January, April, July, and October). On advice of Mr. John Augustine, DOE/PETC, the present report is prepared to cover only two months' work, so that future quarterly reports will be aligned with the conventional reporting schedule.

A significant pressure dependence was observed for the pyrolysis of *n*-tetradecane at 450°C for 30 min. It appears that at least two processes are affected by the reactant pressure, but in opposite directions. The influence of inert gas pressure is dependent on both the initial sample volume and the pressure range. However, when the inert gas pressure is within a certain specific range, the changes in the sample volume have no impact on *n*-tetradecane conversion. Below or above this range, increasing inert gas pressure can either decrease or increase conversion, depending on the sample volume.

Deposit formation from coal-derived JP8C fuel occurs by addition of reactive species at the wall of the reactor as well as by gravitational settling of particles formed in the bulk phase. Stabilization of reactive species by hydrogen donors present in the fuel also occurs simultaneously. Solid formation is determined by the competition among addition of active species to already formed particles, direct addition to the wall, and stabilization by hydrogen donors. The diameter of particles present in suspension at steady state is a function of the concentrations of the intermediates, their diffusion coefficient, the densities of particles and fluid, and the fluid viscosity. Deposit formation from a mixture of 18.45% *n*-tetradecane with JP8C, stressed at 450°C under nitrogen, has an induction period of about four hours, followed by a steady rise in solid formation up to 20 hours, after which little additional deposit is formed.

The addition of a high-surface-area activated carbon PX-21 is highly effective in enhancing the thermal stability of JPTS at high temperatures in both nitrogen and air. A concentration of 50 mg per 10 mL of fuel is sufficient for almost complete suppression of thermal decomposition after stressing for 5 h at 425° in nitrogen and for preventing solid deposition on the reactor walls after stressing in air at 425° for 5 h. A 100 mg/10 mL addition appears to be necessary for preventing solid deposition in air at 450°C for 5 h. The increased stability provided by the activated carbon is explained by the termination of free radical chain reactions on active carbon surfaces.

Deuterated dodecane has been used to probe the hydrogen-donating character of benzyl alcohol. Deuterated dodecane, with and without 5 vol% protonated benzyl alcohol, was stressed at 425°C, 100 psi air, 3 h. The addition of benzyl alcohol leads to the formation of more species in which one or two deuteriums have been replaced by protons, relative to the fully deuterated species. This is strong evidence that benzyl alcohol donates hydrogen and acts as a free radical scavenger.

Quantitative evaluation of the effect of potential stabilizers was done using dodecane as a model compound. For reaction at 450°C, the rate constant for dodecane disappearance decreases in the order dodecane > dodecane + 5% tetralin > dodecane + 5% benzyl alcohol > dodecane + 5% 9,10-dihydrophenanthrene > dodecane + 5% tetrahydroquinoline.

Resinite isolated from Blind Canyon (Utah) bituminous coal contains a substantial amount of occluded material, which appears to be cadinene dimers and triterpenoids, that is easily removed from the polymer backbone. (It should be noted that the state of Utah has 37 billion tons of coal reserves; currently there are 16 commercially viable coal mines in Utah with an annual total production of 22 million tons—resulting in Utah being ranked 13th in U.S. coal production—and an average selling price of about \$22/ton.) Pyrolysis at 710°C increases the yield of bicyclic naphthenes and hydronaphthenes, suggesting that the polymeric make-up of this particular resinite is loosely based on polycadinene. It appears as if dehydrogenation induced by thermal maturation has occurred to some extent throughout the cadinene polymer. Solid-state NMR has shown that approximately three of every fifteen carbons are olefinic, and less than one of the three olefinic carbons is protonated, which again suggests a deviation from the polycadinene structure.

Physical properties calculated from statistical models for a high volatile C bituminous coal agree well with experimental data. (High volatile C bituminous coals, including Illinois No. 6, are likely to be prime candidates for direct liquefaction.) The energetics and physical characteristics found for different models are relatively close to

each other and the variances are small. We have been able to develop a technique that uses the power of the computer to create a number of molecular models for coal using actual quantitative and qualitative experimental data, and to show that the models, from a statistical viewpoint, are a good representation of the coal structure.

Novel bimetallic dispersed catalysts were investigated for promoting liquefaction. These catalysts contain heteronuclear (e.g., molybdenum and cobalt) organometallic clusters. They were tested in liquefaction reactions of a Montana subbituminous coal. The total remaining coal resources of Montana are 472 trillion tons. Montana is ranked 8th in U.S. coal production, with 1991 production over 38 million tons. The structure of the heteronuclear organometallic precursors, in particular the type of ligands bound to the metal species, affects the activity of the resulting bimetallic molybdenum-cobalt sulfided catalyst significantly. For a given precursor, the solvents and methods used for catalyst impregnation also affect coal conversion.

We have begun preliminary discussions with BP America, Inc. regarding possible collaborative efforts with one or more staff members who have had experience in pilot plant refining of oil-shale-derived jet fuels. The intention of such collaboration would be to strengthen the Penn State effort in the areas of developing scalable design data for the projected Phase II pilot plant, assessing the likelihood of conducting coal to jet fuel processing in an existing oil refinery, and economic analyses, as well as the general expertise available from a major oil company.

TECHNICAL PROGRESS

Task 1. Investigation of the Quantitative Degradation Chemistry of Fuels

Condensed-Phase Pyrolysis of Long-Chain Paraffins. Unusual Effects of Sample Volume and Inert Gas Pressure (Contributed by Wei-Chuan Lai and Chunshan Song)

Introduction

Condensed-phase pyrolysis reported here refers to the thermal decomposition of hydrocarbons under elevated pressures. Knowledge of condensed-phase pyrolysis of long-chain alkanes in the temperature range 400–475°C is needed for understanding the behavior of paraffinic species present in petroleum and coal during their co-processing and upgrading. Such information will also be important for developing advanced thermally stable jet fuels for future high-Mach aircraft, where fuel will serve not only as energy source but also as the primary heat sink to cool the airframe and engine, leading to high bulk-fuel temperatures, up to 400–500°C [1-3]. Much of the relevant background has been described elsewhere [4-6]. The motivation of the present study comes from our recent work, in which we found serendipitously that the change in the volume of a sample initially charged also affects its pyrolysis under otherwise identical conditions [4].

With the goal of understanding the pressure dependence of the condensed-phase paraffin pyrolysis, we pyrolyzed *n*-tetradecane using 1–9 mL sample at 450°C for 30 min under initial (cold) N₂ pressure of 0.07–2 MPa (10–280 psig) in 25 mL microreactors. The experimental conditions are characterized by a closed reactor, relatively high and continuously increasing pressure, higher density gas phase or supercritical phases, and long residence time. The temperature of 450°C used in this work is at the lower end compared to most previous alkane pyrolysis studies reported in literature.

Experimental

Aldrich reagent-grade *n*-tetradecane, *n*-C₁₄ (purity: 99+ %) was used in this work. In a typical run, a given amount of *n*-C₁₄ (1–9 mL) was charged into a 25 mL 316 stainless steel microreactor, as described elsewhere [4]. After the reactor was sealed and purged five times, it was pressurized with ultra-high purity N₂ to a selected pressure ranging from 0.069 MPa (10 psi) to 2 MPa (280 psi). The pyrolysis was conducted at 450°C for 30 min in a fluidized sandbath heater. The reactor pressure was monitored after the microautoclave was plunged into the sandbath. The products were separated into gases, liquids, and solid deposits using the procedure described elsewhere [5]. The

gaseous products were analyzed using gas chromatography (GC) with a packed column. The liquid products were identified by capillary gas chromatography/mass spectrometry (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 [5].

Results and Discussion

1. Effect of volume of reactant. Figure 1 shows the molar conversion of n -C₁₄ as a function of the volume of the n -C₁₄ sample initially charged into the reactor. It appears from Figure 1 that the initial sample volume, or the pressure of the reactant, affects the n -C₁₄ conversion in four different ways. First, when the pyrolysis experiments were carried out under a low initial (cold) N₂ pressure of 0.07 MPa (10 psi), increasing sample volume from 1 to 5 mL decreased n -C₁₄ conversion from 35 to 15 mol%. Further increase in sample volume from 5 to 9 mL had little impact on n -C₁₄ conversion. The second case is more complicated, and involves two different regions where the effects of sample volume on n -C₁₄ conversion are opposite to each other. This is the case when the initial N₂ pressure was increased from 0.07 to 0.7 MPa (100 psi). From Figure 1, one can see an increase in conversion with increasing sample volume from 1 to 5 mL, but a decrease in conversion with further increasing sample volume from 5 to 9 mL. The third case is that, when the reactor was pressurized to a certain level with N₂, the change in the initial sample volume has little impact on n -C₁₄ conversion. This is the case when the initial N₂ pressure was 190 psi. Finally, the fourth case is qualitatively opposite to the second case. Namely, when the initial N₂ pressure was 280 psi, the conversion decreases with increasing sample volume from 1 to 5 mL, but increases with further increasing sample volume from 5 to 9 mL.

The fact that increasing the sample volume of n -C₁₄ could increase or decrease its conversion during pyrolysis under otherwise identical conditions (at 450°C for 30 min in the same reactor), and the fact that the influence of sample volume also depends on the initial N₂ pressure, illustrate the complexity of the mechanisms governing the effects of sample volume, or pressure of the reactant.

2. Effect of pressure of inert N₂ gas. Figure 2 shows the influence of pressure of inert N₂ gas on the n -C₁₄ conversion. When the sample volume is 9 mL in the 25 mL microreactor, increasing N₂ pressure from 0.07 to 2 MPa leads to a monotonic increase in n -C₁₄ conversion from about 16 to 50 mol%. However, when 5 mL of sample volume was used, a volcano-shaped curve is obtained: increasing N₂ pressure in the low pressure

range (0.07 to 0.7 MPa) increased *n*-C₁₄ conversion significantly, from about 15 mol% to about 51 mol%, but further increasing N₂ pressure from 0.7 to 2 MPa results in substantially decreased conversion, from 51 to 32 mol%.

The results in Figure 2 reveals that, for a constant sample volume, the trends of changes brought about by increasing the pressure of inert N₂ gas are dependent on both the sample volume range and the pressure range. These results are significantly different from earlier data that the rate constant of alkane pyrolysis increases with pressure up to a maximum at about 100-300 atm [7].

3. Gas-phase or supercritical phase pyrolysis ? It is worth discussing the phase of the reactant under different conditions. The critical temperature (T_c) and critical pressure (P_c) of *n*-C₁₄ are 423.7 °C and 1.5 MPa (218 psi), respectively. Since the reaction temperature of 450 °C is well above the T_c , *n*-C₁₄ could exist in either gas or supercritical state. Based on the critical density of *n*-C₁₄ (0.239 g/cm³) reported in the literature [8] and the volume of the reactor system (about 25 mL), it is likely that at 450°C the reactant exists in supercritical phase when the initial sample volume is 9 mL, and in gas phase when the sample volume is 1 mL and the initial N₂ pressure is 0.07 MPa. With a 5 mL sample, the phase of the reactant at 450°C could be either gas or supercritical, depending on the pressure. In general, pressure affects the density, viscosity, and diffusivity. Pressure change near the critical temperature can change the system from gas-like to liquid-like phases. However, it is difficult to address the effect of pressure on the phase behavior, as the pressure increases continuously during 30 min in the sealed tubing bombs due to the continuous formation of lighter compounds from thermal decomposition. There is no literature information on thermal stability of long-chain alkanes and jet fuels under supercritical conditions. Little is known about the role of inert gas in supercritical fluids at high temperatures. The results in Figure 2 suggest that one can expect a significant pressure dependence of pyrolysis of long-chain alkanes and paraffinic jet fuels under supercritical conditions.

4. Mechanistic considerations. For alkane pyrolysis, high temperature-low pressure conditions generally favor the unimolecular β -scission, while low temperature-high pressure conditions facilitate the bimolecular H-transfer. The present work, however, involves the pyrolysis at the same temperature. It is known that, under the isothermal conditions, the pressure can affect the rate constants according to the Evans and Polanyi's equation:

$$\left[\frac{\partial \ln K}{\partial P} \right]_T = - \frac{\bar{V}_X^\ddagger - \bar{V}_I}{R T} = \frac{-\Delta V^\ddagger}{R T} \quad (1)$$

where $\Delta V^\ddagger$ is the difference in partial molar volumes between transition state ($V_X^\ddagger$) and initial state (V_I) of reagents, known as the activation volume [9]. The activation volume reflects the response of reaction rate to increasing pressure. The formation of a bond between two molecules is accompanied by a reduction in volume. The bond cleavage, however, involves a volume increase and, consequently, $\Delta V^\ddagger$ ($\Delta V^\ddagger = V_I - V^\ddagger$) is positive for the unimolecular decomposition reactions such as radical initiation and β -scission. In contrast to this, $\Delta V^\ddagger$ is negative for bimolecular reactions such as intermolecular hydrogen transfer, radical addition, and radical recombination reactions. According to the transition state theory [8], the rate constants of bimolecular reactions should increase with pressure, while those for unimolecular reactions should decrease with pressure.

Since both inert gas and reactant are present, a fundamental question that arises is how the molecules experience pressure. Literature information on the pressure effects of free radical reactions during hydrocarbon pyrolysis is still very limited and contradictory [7,10-13]. In the present work, the complexity of the response of n -C₁₄ conversion to the sample volume (Figure 1) and N₂ pressure (Figure 2) at the same temperature of 450°C for the same duration suggests that the n -C₁₄ pyrolysis is sensitive to the pressures of both the reactant and inert gas at the temperatures near its critical point, and the pressure effects of the reactant and inert gas seem to be interdependent. At least two different radical reaction processes are affected by the pressure in opposite directions, giving rise to the unusual reversed volcano- and volcano-shaped and linear relationships. The present results also provided experimental evidence that activation volumes ($\Delta V^\ddagger$) of some reactions involved in n -C₁₄ pyrolysis are very sensitive to pressure changes near critical point of n -C₁₄.

Summary

The present results clearly showed that there is significant pressure dependence of n -C₁₄ conversion during its pyrolysis at 450 °C for 30 min. There are unusual volcano-shaped and reverse volcano-shaped curves for the relation between n -C₁₄ conversion and the initial sample volume, which is translated into pressure of the reactant upon heat-up. It appears that at least two processes are affected by the reactant pressure in opposite directions. The influence of inert gas pressure is dependent on both the initial sample volume and the pressure range. However, when the inert gas pressure is within a certain

specific range, the changes in the sample volume have no impacts on n -C₁₄ conversion. Below or above this range, increasing inert gas pressure can either decrease or increase n -C₁₄ conversion, depending on the sample volume. A number of fundamental questions remain to be answered. Further work is now in progress.

References

1. Roquemore, W.M., Pearce, J.A., Harrison III, W.E., Krazinski, J.L., and Vanka, S.P. Am. Chem. Soc., Div. Petrol. Chem. Prepr., 1989, 34 (4), 841-849.
2. Moler, J.L.; Steward, E.M. Am. Chem. Soc., Div. Petrol. Chem. Prepr. , 1989, 34 (4), 837-840.
3. Lee, C.M.; Niedzwiecki, R.W. Am. Chem. Soc., Div. Petrol. Chem. Prepr., 1989, 34 (4), 911-919.
4. Song, C.; Eser, S.; Schobert, H.H., Hatcher, P.G. Energy & Fuels, 1993, 7, 234-243.
5. Lai, W.-C.; Song, C.; Schobert, H.H.; Arumugam, R. Am. Chem. Soc. Div. Petrol. Chem. Prepr., 1992, 37 (4), 1671-1680.
6. Song, C.; Lai, W.-C.; Schobert, H.H. Am. Chem. Soc. Div. Petrol. Chem. Prepr., 1992, 37 (4), 1655-1663.
7. Fabuss, B. M.; Smith, J.O.; Satterfield, C.N. Adv. Petrol. Chem. Refin., 1964, 9, 158-201.
8. Yaws, C.L.; Chen, D.; Yang, H.-C.; Tan, L.; Nico, D. Hydrocarbon Processing, 1989, No.7, 61-64.
9. Isaacs, N.S. Liquid Phase High Pressure Chemistry. Wiley: New York, 1981, Chapter 4, pp. 181-353.
10. Doue, F.; Guiochon, G. Can. J. Chem., 1969, 47, 3477-3480.
11. Domine, F. Energy & Fuels, 1989, 3, 89-96.
12. Domine, F. Org. Geochem., 1991, 17, 619-634.
13. Mallinson, R.G.; Braun, R.L.; Westbrook, C.K.; Burnham, A.K. Ind. Eng. Chem. Res., 1992, 31, 37-45.

Task 2. Investigation of Incipient Deposition

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

Introduction

This work is the continuation of our study of growth and deposition of particles during heating of coal-derived (JP8C) aviation gas turbine fuels. Deposit formation occurs by addition of reactive species at the wall of the reactor as well as by gravitational settling of particles formed in the bulk phase. Stabilization of reactive species by hydrogen donors present in the fuel also occurs simultaneously. Solid formation is determined by the competition among addition of active species to already formed particles, direct addition to the wall and stabilization by hydrogen donors. The diameter of particles present in suspension at steady state is a function of the concentration of the intermediates, their diffusion coefficient, the densities of particles and fluid, and the fluid viscosity. In this study an attempt was made to determine if the formation and deposition reactions of a particular class of reactive species could explain the observed rate of deposit growth on the walls of reactor as well as the rate of formation of suspended particles. Tetradecane was selected as the precursor for reactive species, added in varying amounts to coal-derived jet fuel.

Measurement

Mixtures of tetradecane and coal-derived jet fuel containing 18.45 wt% tetradecane were stressed at 450°C under an initial nitrogen pressure of 0.69 MPa. The tubing bomb reactors were purged with nitrogen eight times to remove residual oxygen. The stress time was varied from 2 to 24 hours. The deposits formed on the bottom, side walls, and top of the reactor were weighed separately. These measurements are shown in Figures 3a, 3b, and 3c respectively. The mass of suspended particles obtained by filtration is shown in Figure 3d.

Discussion

From Figure 3 it can be seen that deposit formation from this mixture has an induction period of about four hours, followed by a steady rise in solid formation up to twenty hours, after which little additional deposit is formed. One reason for measuring particle concentration as a function of time was to examine whether the concentration would become steady at long times, the steady value determined by the competition

between particle formation and deposition on the bottom of the reactor. In spite of the close spacing of the measurements, the time dependence of the particle concentration cannot be established from these data. Additional measurements at short, long and intermediate times are needed to resolve this question. Measurements of particle size distribution will also be made during this experiment. The next step in our study will be to determine the impact of deliberate addition of H-donors and alkylated benzenes on the rates of formation of suspended particles and deposits. A kinetic model for growth of particles and solid formation will be constructed using measurements of the concentrations of deposit precursors and H-donors as function of time.

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

1. 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, JPTS and Jet A-1 fuels to study the effects of carbon surfaces on solid deposition and stability of fuel samples. It appears that the surface area of added carbons is the most important parameter which determines the effectiveness of blocking solid deposition and degradation of the jet fuel samples [1].

We reported some preliminary results for adding the high surface area activated carbon PX-21 (N_2 BET 3000 m^2/g) to JPTS and A-1 jet fuels during stressing. These initial results show that we can significantly reduce the amount of added activated carbons necessary to suppress thermal degradation, if we use a high surface area carbon. The data for thermal stressing of Jet A-1 with 200 mg PX-21 and JPTS with 100 mg PX-21 per 10 ml of both fuels at 450°C for 5 h in a nitrogen atmosphere were presented in our previous quarterly report [1]. The high surface area of activated carbons added to jet fuel inhibits thermal degradation and particularly the formation of insoluble solids on reactor surfaces. It appears that the activated carbon surfaces are effective in terminating free radical chains through stabilization of reactive intermediates as well as selective catalysis of cracking reactions. These interactions with the carbon surface lead to the formation of low-molecular-weight alkanes (C_3H_8 through C_6H_{14}), preserving some long-chain alkanes and decreasing the concentration of alkylated aromatics, polyaromatics and alkylated polyaromatics, which are the most probable precursors to solid deposits [2].

In this report, we present the the results obtained from stressing JPTS with PX-21 in an air atmosphere at two different temperatures to study the effectiveness of adding an activated carbon in the presence of oxygen.

Experimental

Thermal stressing experiments were carried out on 10 mL samples of JPTS jet fuel mixed with 100 mg activated carbon PX-21 at 450°C for 5 h in an air atmosphere. A 10 ml JPTS with 50 mg PX-21 was also stressed at 425°C in air and nitrogen atmosphere. PX-21 carbon has a BET N₂ surface area of 3000 m²/g and has been supplied by Amoco Oil Company.

The jet fuel sample and activated carbon were placed in the microautoclave reactor which was purged with UHP grade N₂ five times to minimize the pressure of dissolved oxygen and finally pressurized to 100 psi with air or nitrogen.

Liquid products obtained after stressing of JPTS alone and mixed with PX-21 as well as JPTS neat were characterized by gas chromatography. A Hewlett-Packard 5890 Series II gas chromatograph with a silica capillary column was used, and a quantitative analysis of the liquid products was carried out using calibration curves obtained from external standards. A Hewlett Packard 5890 gas chromatograph interfaced with a HP 5971A mass selective detector was used for qualitative analysis of the liquid products.

The deposits obtained after thermal stressing of JPTS alone and with the activated carbon PX-21 before and after stressing with JPTS were examined using a polarized-light microscope (Nikon-Microphot FXA).

Results and Discussion

1. Thermal stressing of JPTS mixed with 100 mg PX-21 at 450°C in air atmosphere. Relatively severe thermal stressing experiments of JPTS jet fuel alone and mixed with 100 mg PX-21 in air atmosphere show that the addition of high-surface-area activated carbon influences the chemistry and mechanisms of thermal degradation. As was observed with the stressing experiments in a nitrogen atmosphere, differences were observed in the appearance (e.g., color) of the liquid products obtained after stressing and particularly the inhibition of solid deposition on reactor walls upon carbon addition in an air atmosphere.

Figure 4 shows the differences in the appearance of the liquids obtained after thermal stressing of JPTS alone jet and mixed with 100 mg PX-21 in air atmosphere. Although both liquids are have a dark brown color, the liquid produced in the presence of PX-21 has a distinctly lighter color. Both liquids appear much darker compared to the

stressing products obtained from the corresponding experiments carried out in a nitrogen atmosphere. It should be noted, however, that despite the dark-colored liquid obtained from JPTS PX-21 no noticeable deposit was observed on the reactor walls.

Table 1 shows the yield of the liquid and solid products and the pressure build up from thermal stressing experiments of JPTS jet fuel alone and with 100 mg PX-21 at 450°C for 5 h in air and nitrogen atmospheres. It can be seen that thermal stressing of JPTS with 100 mg PX-21 at 450°C in nitrogen as well as in air does not lead to the formation of carbonaceous deposits on reactor walls. It is interesting to note that the amount of solid deposits produced after thermal stressing in air is not very different from that obtained in nitrogen after 5 h at 450°C (63 mg in nitrogen and 70 mg in air). These results show, once again, that JPTS is a considerably more stable fuel than JP-8 in both nitrogen and air atmospheres. It is also important to point out that at high temperatures where the pyrolysis is the dominant mechanism of degradation the presence of high concentrations of oxygen does not have a measurable effect on the yield of carbonaceous solids. As different from the results obtained with JP-8 in the presence of other activated carbons, higher liquid yields and lower gas pressures were obtained from JPTS in both nitrogen and air atmospheres in the presence of PX-21. It is clear that the interactions between the JPTS and PX-21 surface are different from those of JP-8 and other carbon surfaces. As discussed below, no carbonaceous deposit was observed on the surfaces of PX-21 stressed with JPTS, whereas JP-8 produced deposits on the added activated carbons. In addition, the reduced final gas pressures upon addition of PX-21 to JPTS indicate a dramatic reduction in the extent of cracking reactions leading to light hydrocarbon gases. These results show that the higher stability of JPTS is substantially enhanced upon adding PX-21 prior to thermal stressing.

Table 1 also shows that the weight gain of the added solids after thermal stressing. The observed weight gain can be due to gas adsorption, liquid adsorption, or solid deposition on activated carbon surfaces in addition to carbonaceous solids formed in suspension from the reacting fluids. The optical microscopic examination shows no apparent deposition on the PX-21 surface and no fluid-phase solids mixed with the activated carbon surfaces. Therefore, the observed weight gain should be mostly due to gas and liquid adsorption and possibly to the thin layer of deposits with a thickness below the resolution of the optical microscope ($\approx 0.5 \mu\text{m}$). Table 1 shows twice as much weight gain of PX-21 used in an air atmosphere as that obtained in nitrogen. Chemisorption of oxygen as well the adsorption of oxygenated species on the activated carbon surface are probably responsible for the higher weight gain observed upon stressing in air.

2. Microscopic examination of the deposit and activated carbon PX-21 after thermal stressing with JPTS jet fuel. Figure 5 shows the polarized-light micrographs of PX-21 activated carbon after thermal stressing with JPTS at 450°C for 5 h in air atmosphere. Figure 5a represents essentially the microstructures of PX-21. The anisotropic microstructure of PX-21 is unusual for activated carbons. As can be seen from Figure 5a, there is no apparent deposition on the activated carbon surface. The higher magnification micrograph (Figure 5b) shows a single small particle of pyrolytic carbon deposited on reactor wall.

Figure 6 shows the micrographs of the deposits obtained from stressing JPTS alone at 450°C for 5 h in an air atmosphere. The two distinctly different particle morphologies seen in Figure 6 include straight pyrolytic flakes formed by direct gas to solid transformation on a metal surface and layers of deposits formed by the diffusion of carbonaceous droplets nucleated in a fluid phase to the metal surface. The spherules of carbonaceous material on one side of the deposit layers, as seen clearly in Figure 6c, indicate a continuous growth of these deposits by the transport of the liquid-like droplets to reactor surfaces. It can be concluded from the observed microstructures that the precursors to straight flakes are low molecular weight alkanes and/or alkenes (C_1 to C_4), while polyaromatic intermediates lead to the formation of fluid-phase nucleation of liquid-like droplets which diffuse to the reactor walls to form the considerably thicker deposits. It appears that the presence of oxygen promotes the formation of solids through the addition of fluid-phase droplets onto the surfaces.

3. Thermal stressing of JPTS mixed with 50 mg PX-21 at 425°C in nitrogen and air atmosphere. In order to study the effects of PX-21 addition at a lower temperature with a reduced amount of the activated carbon, 10 mL JPTS was stressed with 50 mg of PX-21 at 425°C for 5 h in air and nitrogen atmosphere. Figure 7 shows the difference in the appearance of the liquids obtained with or without PX-21 after thermal stressing in nitrogen and air. The liquids obtained with PX-21 in nitrogen as well as in air have light yellow color while the liquids obtained from JPTS alone have a light brown color in nitrogen and dark brown color in air. No visible deposit was observed on the walls of the reactors after heating JPTS with PX-21, whereas approximately 20 mg of solids were produced in nitrogen and 30 mg of solids in air from stressing JPTS alone.

Figure 8 shows the gas chromatograms of the unstressed JPTS, and of the liquid products obtained from JPTS stressed alone and with PX-21 at 425°C for 5 h in nitrogen. The chromatogram in the middle in Figure 8 shows that the liquids obtained from the JPTS stressed alone contains high concentrations of short-chain normal and branched alkanes (C_4 - C_8), C_5 and C_6 cycloalkanes and some alkenes which are produced by

cracking reactions. Their concentration in the liquid obtained after thermal stressing of JPTS mixed with PX-21 is negligible, as shown in the chromatogram at the bottom of Figure 8. It can be seen that in the chromatograms of Figure 8 that the liquids produced after stressing with PX-21 show very little change in chemical composition compared to the unstressed fuel, indicating the dramatic effect of PX-21 addition on fuel stability in nitrogen atmosphere..

Figure 9 shows the chromatograms of the corresponding liquids obtained after stressing in air. Different from the trends observed in Figure 9, the liquids obtained in the presence of PX-21 show cracking into short-chain normal and branched alkanes and other low molecular weight hydrocarbons, but at substantially lower extents compared to the liquids obtained from JPTS stressed alone. It appears that the same concentration of PX-21 as in nitrogen stressing is not sufficient for the almost complete suppression of cracking reactions upon stressing in nitrogen (Figure 8). The observation that no solid deposit is produced after stressing with PX-21 in air still shows that, even at the present additive concentration, solid deposition is prevented.

4. Microscopic examination of the deposits and PX-21 activated carbon after thermal stressing of JPTS at 425°C in nitrogen and air. Figure 10 shows the optical texture of the carbonaceous solid obtained after thermal stressing of JPTS alone at 425°C in nitrogen atmosphere. The deposits appear as relatively thick flakes with pyrolytic carbon texture.

Figure 11 shows the polarized-light micrographs of the carbonaceous solid obtained after thermal stressing of JPTS at 425°C in air atmosphere. Compared to the deposits obtained in nitrogen, air stressing produces thinner flakes with a finer texture of pyrolytic carbon..

Conclusions

The addition of a high-surface-area activated carbon PX-21 is highly effective in enhancing the thermal stability of JPTS at high temperatures in both nitrogen and air atmospheres. A concentration of 50 mg per 10 mL of fuel is sufficient for almost complete suppression of thermal decomposition after stressing for 5 h at 425°C in nitrogen and for preventing solid deposition on the reactor walls after stressing in air at 425°C for 5 h. A 100 mg/10 mL addition appears to be necessary for preventing solid deposition in air at 450°C for 5 h. The increased stability by activated carbon addition is explained by the termination of free radical chain reactions on active carbon surfaces.

References

1. Schobert, H. H., Eser, S., Song, C., Hatcher, P., Walsh, P., Coleman, Advanced Thermally Stable Jet Fuels, Technical Progress Report, November 1992-January 1993.
2. Song, C., Peng, Y., Jiang, H., and Schobert, H. H., Preprints, Div. Pet. Chem., ACS Symposium on Structure of Jet Fuels III, San Francisco, April 5-10, 1992.

2. Surface Effects on the Formation of Carbon Deposits—A Literature Review (Contributed by Jun Li)

Introduction

Jet fuels are mixtures of hundreds of hydrocarbons including paraffins and aromatics. According to thermodynamics [1], these hydrocarbon species could undergo essentially a hydrogen redistribution process under severe thermal stressing, resulting in a hydrogen-rich gas/liquid phase and a hydrogen-poor carbonaceous solid. Such a severe thermal loading (e.g. 450 °C) is anticipated in developing the fuel system of high-performance aircraft [2, 3]. Carbonaceous deposit formation is a minor reaction relative to the main fuel degradation but is of great importance in that it can lead to the malfunctioning of the fuel system [4]. The rate of deposit formation, however, depends on the fuel and the environment the fuel serves. A slow deposit formation process may be catalyzed by certain types of metal surfaces present in the fuel system, or, hopefully, deposit formation could be inhibited by the judicious selection of the fuel and its service conditions. Obviously, this relies on an understanding of the mechanisms of catalytic and non-catalytic deposit formation.

Ultimately, carbon deposits can form via two opposite routes: decomposition of the hydrocarbons to elemental carbon and hydrogen, or polymerization to large planar polycyclic aromatic hydrocarbons (PAHs) which then nucleate and grow to carbonaceous deposits. As we shall see, catalytic carbon deposits probably form by the decomposition route, whereas non-catalytic carbon deposits most likely form by the polymerization route.

A critical factor determining the formation of catalytic or non-catalytic carbon deposits is the characteristic of the substrate surface. A non-catalytic surface may affect the heat or mass transfer in the system and act to collect the carbon deposit formed in the bulk phase. In contrast, a catalytic surface could, in addition, interact with the bulk phase, promote the deposit formation, and finally be deactivated to a non-catalytic surface due to

the encapsulation by carbon deposits. Thus, it is particularly interesting to see the effects of a metal surface on the formation of carbonaceous deposits.

The primary goal of this section is to review the literature on the mechanisms of carbonaceous deposit formation in the jet fuel range. In addition, the review area is extended to cover catalytic and non-catalytic deposit formation from related light or heavy hydrocarbons, because (i) there is only limited mechanistic information of deposit formation from jet fuels, and (ii) there may be great similarities in mechanisms of deposit formation despite the differences in their original compositions. Contrast of catalytic and non-catalytic deposit formation is also highlighted. To avoid being overwhelmed by the vast amount of literature due to the extension, we will confine ourselves to the coverage of the *mechanisms* with a special attention to the effects of *surfaces*.

Mechanisms of Carbonaceous Deposit Formation from Jet Fuels

1. Chemistry of Deposit Formation. Early studies on deposit formation from thermally stressed jet fuels have investigated a wide range of reactants as well as variables. Air-saturated or deoxygenated jet fuels and model compounds were stressed under pressures from sub-atmospheric up to 340 atm and temperatures from ambient up to 650 °C in specially designed flow reactors or a Jet Fuel Thermal Oxidation Tester (JFTOT) [3, 5-14]. The rate of deposit formation from air-saturated jet fuels or model compounds was found [8-10, 14] to show a complex relationship with temperature (see Figure 12). In general, the rate rises with increasing temperature, drops sharply in a transition zone covering an approximate 350–425 °C range, and then again increases with rising temperature. This has been explained by a dual mechanism of deposit formation: liquid phase autoxidation at low temperatures, gas phase or supercritical pyrolysis at high temperatures, and a combination of these two in the transition region.

The mechanism of autoxidation reactions can be shown as follows [10]:

(2.5)

Carbon deposition was closely associated with hydroperoxide formation or decomposition [10]. A large amount of oxygen (15–30 wt %) was found in typical autoxidative hydrocarbon fuel deposits. Lesser but significant amounts of sulfur and nitrogen were also detected in the deposit. Scanning electron microscopy (SEM) showed spherical deposits form in the bulk phase [11, 15] and, because of their polar nature, they were insoluble in the bulk fuel and tended to settle out as spheres on the tube surface. Taylor [8] concluded that in liquid phase autoxidative deposit formation it is the change in solvent character resulting from the incorporation of oxygen, nitrogen, and sulfur into the deposit species which is important rather than the increase in molecular weight.

The sharp drop in the rate of deposit formation was attributed to a reduction in the autoxidative reaction rate caused by a lowering of the concentration of reactive species as the system passes from a liquid phase to a vapor phase [8]. Certain types of jet fuel could reach the supercritical state, depending on the pressure (e.g., $T_c = 410\text{ }^{\circ}\text{C}$, $P_c = 22.4\text{ atm}$ for JP-5). Thus, the sharp drop in rates would be an effect of the transition between the liquid phase and the supercritical vapor phase.

At higher temperatures, vapor phase pyrolysis dominates the system, and the reactions are much more complicated. Mechanisms of deposit formation in this regime are not well understood. It is believed [16] that deposits form as a result of free radical reactions including cyclization, aromatization, condensation, and polymerization reactions. In addition, the deposition process involves gas phase (pyrolytic carbon) and liquid phase (mesophase) carbonization [17]. Research on the mechanisms of deposit formation from jet fuel pyrolysis is still underway.

Although most of the studies focus on the homogeneous reactions leading to deposit formation, the possible catalytic effects of metal surfaces have been a real concern.

2. The Role of Surface Composition. The possible heterogeneous catalytic effects produced by various substrate metals on deposit formation from jet fuels have been studied by many investigators [4,9,12,18-26]. Direct comparison of rate of deposit formation measured by different investigators can not be successful. Nevertheless, copper and its alloys have consistently been found to be the most deleterious metal in that it promotes deposit formation with aerated fuels at temperatures up to $427\text{ }^{\circ}\text{C}$. This is true in the ASTM-CRC coker test for aviation kerosene (Avtur 50) [18], in a specially designed Kinetic Unit test for five different jet fuels [19], and in a modified JFTOT for Jet A [22]. Certain titanium alloys (likely candidates for supersonic aircraft) also affect the rate of deposit formation, and the effect increases with the content of vanadium in the

alloy. However, the effects of other materials, e.g., Al, Au, Mg, Ni, stainless steel, on deposit formation are controversial. Taylor [19], Hazlett, *et al.* [9], and Baker, *et al.* [22], found that the rates of deposit formation were the lowest and the same using Al tubes and stainless steel tubes. In contrast, Wong and Bittker [21], Kendall and Mills [23], and Stavinoha, *et al.* [26], found that using stainless steel tubes increased the rate of deposit formation compared to aluminum tubes; in some cases, the rate doubled if the aluminum tube was replaced by a stainless steel tube [23]. Hazell, *et al.* [24], using Auger electron spectroscopy (AES) combined with argon ion bombardment (AIB), found that the segregation of magnesium from the bulk of the aluminum tube to its surface oxide dramatically reduced the thickness of deposit, and coating the aluminum tube with MgO confirmed that it did inhibit the deposit formation. On the contrary, Stavinoha, *et al.* [26] found that deposit on an Mg coated tube was thicker than on an Al coated tube as measured by Auger ion milling. The morphologies of deposits were different: hemispherical deposits on the magnesium surface and flat platelet type deposits on the other metal surfaces (Al, SS, Au). Clearly, the inhibition of deposit formation by magnesium needs to be verified. Another interesting finding was that an Ni-plated tube significantly reduced the carbon deposition rate (an order of magnitude reduction) compared to a copper tube at tube wall temperatures between 600 and 800 K, and 136 atm for kerosene type fuel RP-1 [12].

It should be noted that different thermal conductivities of different metals would cause different temperature gradients along reactor walls (i.e. different local fuel temperatures), thereby affecting the deposit formation. This point will be discussed in more detail in the following subsection

Characterization of the deposit, particularly across the depth on the surface, could be helpful in interpreting the interaction of the metal substrate and the stressed fuel. Scanning electron microprobe (SEMP) photographs [12] showed a "dendritic" morphology of deposit formed from commercial propane fuel on copper tube at 700 K. The dendrite contained a high concentration of copper, suggesting that the tube material was forced up and away from the surface. In a separate study [26], metal ions were also suggested to be included in the bulk of deposit, affecting the dielectric strength of the deposit, and resulting in different thickness measurements by Auger ion milling and by dielectric strength method. Chemical composition also varies with the location. Limited data showed that the proportion of aromatic to aliphatic hydrocarbons increased towards the maximum tube temperature and also closer to the tube surface in a deposit [25].

The reasons why heterogeneous surfaces of metals and metal oxides are capable of increasing the rate of reaction of hydrocarbon with oxygen in the liquid phase are by

no means understood. Taylor [19] noted that the metal oxide surface could catalyze the autoxidation reaction by generating a free radical in the following manner:

Those elements would be active which could undergo easy reduction by one-electron transfer, just as observed that the most active surfaces were copper-and vanadium-containing alloys. He also pointed out that the oxides of copper and vanadium were well known as active heterogeneous oxidation catalysts. Since it has been shown that jet fuels undergo autoxidation at low temperatures and pyrolysis at high temperatures, a reasonable extension of Taylor's suggestion would be to examine the effects of those metals that are used as hydrogenation or dehydrogenation catalysts on the deposit formation at high temperatures. These metals include Fe, Ni, Pt, etc. However, no systematic studies of the effects of these metals on high temperature (>400 °C) deposit formation from jet fuels or model compounds have yet been reported.

3. The Role of Surface Temperature. It was indicated in subsection 1 that temperature had a complex impact on the rate of deposit formation from jet fuels and this impact was further interpreted as causing different reaction mechanisms, i.e., autoxidation at low temperatures and pyrolysis at high temperatures. This conclusion could have significant practical importance because it implies that the temperature window of low rate of deposit formation between the autoxidation region and the pyrolysis region could be an optimum operating condition for the jet fuel system. However, recent studies [27, 28] showed that this conclusion should be treated more cautiously.

As described in subsection 2, this conclusion was drawn from studies using flow reactors. In a flow reactor, heat transfer phenomena determine that fuel and wall would have different temperatures. It is thus necessary to distinguish the effects of fuel temperature and/or wall temperature. Most of the flow reactor studies used constant heat flux method [9, 29-31] and correlated the rate of deposit formation with the initial maximum wall temperature. In this method (see Figure 13), fuel flows over a long thin-walled tube (usually stainless steel) that is resistant-heated. The total heat flux is kept constant by controlling the inlet and outlet fuel temperature constant. As the deposit builds up inside the wall, the outer surface temperature increases dramatically. This increased wall temperature will in turn affect the local fuel temperature due to the heterogeneity of the deposit radially and axially. Moreover, the temperature difference between the inlet and outlet fuel could be very high (e.g., 450 K for JP-5 fuel at 27.2 atm [29]). Consequently, the observed variation of deposition rate actually results from the

combined effects of fuel and wall temperatures, fuel temperature probably being more important.

Chin *et al.* have recently developed a constant surface temperature method [27, 28] (see Figure 14). In this method, the fuel temperature is controlled by a fuel preheater, whereas the wall temperature is kept constant during the test by jacketed W/cartridge heater. Tests with JP-8 showed that an increase in wall temperature always increased the rate of deposition at a given low fuel temperature ($<300\text{ }^{\circ}\text{C}$). In addition, fuel temperature had a more profound effect on thermal stability. The deposition rates were relatively low for fuel temperatures below around 400 K, but rose steeply with the increase in fuel temperatures above around 500 K.

With the constant surface temperature method, two other sets of experiments should be carried out: (1) increasing the fuel temperature; (2) broadening the temperature difference between inlet and outlet fuel to verify the dual reaction mechanisms proposed using the constant-heat flux method. This would be difficult because the reaction zone in the system can not be well defined at high fuel temperatures. In this regard, static reactors may be preferred.

Despite the skepticism raised by the constant surface temperature method, the decreasing rate of deposit formation at higher temperatures has been observed by many independent workers. Interestingly, a similar negative temperature region has also been found in gas phase carbonaceous deposit formation from pyrolysis of low hydrocarbons on metal surfaces [32, 33]. It was attributed to the reduced chemisorption rate on metal surface at elevated temperatures and also a mechanism change from heterogeneous catalytic carbon formation to gas phase pyrolytic carbon formation. Although that system is very different from jet fuel thermal stressing, it would be interesting to see if there are similar catalytic effects of metal surface on deposit formation in our jet fuel study.

From the above discussion, it is clear that there is a lack of systematic studies on the effects of metal surfaces on deposit formation from jet fuel thermal degradation and pyrolysis, let alone the fundamental mechanistic studies on the deposition process. As indicated in the Introduction, we will now expand the review base.

Mechanisms of Catalytic Carbon Formation

Carbon formation from light hydrocarbons on metal surfaces, especially on Group VIII metal surfaces, has been extensively investigated, mainly because of its importance in many industrial processes and the recent attempt to produce the desired carbon products, i.e., vapor-grown carbon fibers [34-37]. Depending upon the reaction conditions, different forms of carbon deposits have been observed. McCarty *et al.* [38],

using temperature-programmed surface reactions with hydrogen and water, have identified seven different states of carbon formed by exposing C_2H_4 to alumina-supported nickel catalysts over a wide temperature range. They classified these carbons in the order of reactivity as a', a (reactive and chemisorbed carbon), b (carbon film), g (nickel carbide), d', d (filamentous and encapsulating carbon), and e (platelet carbon). However, more intuitively and frequently, catalytic carbon deposits have been characterized according to their morphologies as laminar graphitic carbon, non-oriented polycrystalline carbon, and filamentous carbon [39]. Among these, filamentous carbon has been the most thoroughly studied.

1. The Mechanism of Filamentous Carbon Formation. Filamentous carbons have been observed in the decomposition of light hydrocarbons over ferromagnetic metals at temperatures between 600 to 1000 K [33, 40-44]. They are usually long and thin (up to 7 mm long and 0.1 mm wide) and have a hollow core and a metal particle at the tip; the particle usually has a pear shape and the same size as the filament diameter. The carbon is mainly turbostratic with the basal planes preferentially oriented parallel to the filament axis [45]. Filamentous carbon is of particular interest because the temperature range within which it is formed coincides with the range where important industrial processes, e.g. Fischer-Tropsch synthesis, methanation, and steam-reforming, are usually carried out. It is also the most detrimental form of carbon on a catalyst surface.

Baker *et al.* [40, 42, 44] based on studies of filamentous carbon formation from acetylene over Ni, Fe, Co, and Cr using controlled atmosphere electron microscopy (CAEM), proposed a mechanism which is now referred to as the "classical" model [46]. This classical model (see Figure 15A) contains the following steps:

- (i) detachment of a metal particle;
- (ii) adsorption of gas at the metal surface followed by decomposition reactions leading to chemisorbed carbon species;
- (iii) dissolution in and diffusion of carbon species through the metal particle to active growth areas such as grain boundaries;
- (iv) precipitation of the carbon species to form the body of the filament;
- (v) migration of carbon species remaining on the metal surface around the particle to form the skin component of the filament; and
- (vi) encapsulation of metal particle due to the build-up of excess surface carbon, ending further growth.

A variation to this model is the formation of filamentous carbon by an extrusion mode, in which filaments do not grow from a free particle but from a particle attaching to

the support surface. The mechanism (see Figure 15B) proposed by Baker and Waite [47] assumes that in the Fe-Pt/C₂H₂ system, Pt segregates to the particle surface, and decomposition of C₂H₂ occurs predominantly on the Pt-rich region. A consecutive process takes place to transport carbon through the catalyst: rapid diffusion through Pt followed by slower diffusion through the Fe component to be precipitated on the upper surface of the particle as a filament.

One of the key pieces of evidence leading to these models came from the kinetics study. Baker *et al.* [42, 48] showed that the activation energy of the growth of filamentous carbon correlated for Ni, Fe, Co, etc. with the activation energy of carbon diffusion in the metal (see Table 2), and therefore the diffusion of carbon through the metal particles (bulk diffusion) was considered as rate determining for filament growth.

The rate of carbon deposition has a complex relationship with temperature as shown in Figure 16 [49]. Trimm divided the temperature into three regions: low temperature (LT) (<550 °C), intermediate temperature (MT) (≈550–650 °C), and high temperature (HT) (>650 °C). In the LT region, the rate increases with temperature; diffusion of carbon through nickel appears to be the rate-determining step (rds) for alkenes and acetylene. In the MT region, the rate decreases with increasing temperature, and also depends on the concentrations of the gaseous reactants. This was explained in terms of adsorption effects in a rate-determining surface reaction: $E_{A \text{ app}} = E_{A \text{ true}} - \Delta H_{\text{ads}}$, where ΔH_{ads} is the heat of adsorption. In the HT region, the rate increases again with temperature. It was suggested that gas-phase pyrolysis reactions were involved in this region, producing soot particles on the surface.

Coming back to the classical model, it is necessary that a concentration gradient of carbon atoms from the leading face to the trailing face of the particle exists in order to drive the diffusion step. Baker *et al.* suggested that the driving force for the diffusion was a temperature difference created by the exothermic catalytic reaction supplying the surface carbon atoms. However, filament growth was also observed in cases where the surface reaction was endothermic [33]. Baker *et al.* [50] have replied that saturated hydrocarbons are known to decompose via their dehydrogenated analogs. Decomposition of the latter compounds is exothermic, and consequently, a mechanism involving thermal diffusion would not be contravened. This explanation, however, assumes separate sites where only the endothermic dehydrogenation takes place. Moreover, Holstein and Boudart [51] showed by calculations that the temperature difference that could be generated between a metal particle and a support when an exothermic surface reaction took place on the metal particle of a supported catalyst was negligible (less than 0.1 K). Although recently Yang and Chen [52] suggested that for endothermic decomposition

(such as CH₄, C₄H₁₀, C₆H₁₄, C₄H₈) the heat may be supplied by the radiation from the surroundings to the gas/metal interface, which results in a temperature gradient between gas/metal interface and the cooler metal/graphite interface to sustain the bulk diffusion, thermal ways of establishing the necessary gradient have received less attention [53].

Rostrup-Nielsen and Trimm [33] proposed an alternative concentration-driven mechanism for filament growth. Referring to reported literature data [54, 55], they deduced that carbon species of different origins have different solubilities. Supersaturation of carbon in nickel could occur at the gas/nickel interface when the activity of carbon in the gas phase exceeded unity; whereas at the nickel/filament interface the activity of carbon is very close to unity. The resulting concentration gradient is thought to be responsible for carbon transport. However, because of the significant scatter in the reported solubility data [56, 57], the physical basis for this hypothesis of natural concentration-driven mechanism remains to be proven.

Further advances in explaining the driving force for the diffusion came from thermodynamic studies. For a simple gas mixture like CH₄/H₂, one can calculate the critical composition for carbon deposition at a given temperature and pressure:

A mixture with greater CH₄ content than the critical value should lead to carbon deposition. However, Rostrup-Nielsen ^[41], Manning *et al.* [58, 59], and De Bokx *et al.* [60] all observed that carbon did not deposit even when its critical composition was exceeded. The Gibbs free energy change for the (filamentous) carbon formation reaction is greater than that for the β -graphite formation reaction. The difference, $\text{DG}_c = -RT \ln (K_p / K_{p(\beta\text{-graphite})})$, was found to be 1.5 and 3.0 kcal/mol at 800 and 700 K ^[41] ($\text{DG}_c = 0$ when $T > 1000$ K). Here K_p is the equilibrium constant $K_p = P_{\text{H}_2}^2 / P_{\text{CH}_4}$, and $K_{p(\beta\text{-graphite})}$ is the equilibrium constant assuming C in β -graphite state.

Two explanations emerged to account for this deviation from graphite. First, Rostrup-Nielsen estimated the energy contribution of structural defects (from graphite), as well as the curved surface of filamentous carbon. It was shown that if the DG_c was altered by such an amount, then the experimental observation could be rationalized. However, De Bokx *et al.* pointed out that these energy differences (i.e. crystalline imperfections and surface energy due to curvature) would be observed as changes in the standard heat of reaction (DH_c) rather than standard free energy changes in the reaction (DG_c). Consequently, this DH_c could not match the values they had measured experimentally ($\text{DH}_c = 40$ kJ/mol). Later, Alstrup [46] included a third elastic energy term which was first introduced [61] to explain the tubular and hollow nature of filamentous carbon. This elastic energy arises from bending the basal planes of graphite

to form the near cylindrical structure of filaments. Alstrup showed that when all three terms were included, the change in the standard heat of reaction was large enough to match the heat of reaction values obtained experimentally by De Bokx *et al.*

Second, the deviation has been explained by the formation of a "metastable" carbide. Manning *et al.* [58, 59] and Sacco *et al.* [62, 63] found that the experimentally observed critical composition for filament growth nearly coincided with the critical composition calculated for the formation of $\theta\text{-Fe}_3\text{C}$, and similar results for Ni and Co. The observed catalyst weight increase was much greater than could be accounted for by the formation of a stable carbide. They suggested that carbon was deposited as a metastable carbide intermediate. Later, Geus and collaborators [45, 60, 64] reported that the standard heat of reaction was very nearly equal to the standard heat of formation of Ni_3C and $\theta\text{-Fe}_3\text{C}$:

On the basis of this observation and the results of the magnetic measurements, they concluded that the active catalyst was an intermediate, unstable carbide.

The two recent models proposed by Geus *et al.* and Alstrup are schematically shown as Figure 17 [53]. For Geus' model (Fig. 17a), the catalyst is a single phase whose composition varies from the side in contact with the gas to the side in contact with the filament. The catalyst bulk is a single carbide phase, Fe_xC , where x is smaller at the leading face than at the trailing face. For Alstrup's model (Fig. 17b), the key feature is that a surface carbide, only a few atomic layers thick, is proposed to form on the leading face of the catalyst. The rate-determining step is still the transport of carbon through the catalyst bulk, but the surface carbide fixes the carbon content at the leading face of the bulk of the catalyst and provides the driving force for bulk diffusion of carbon.

Lund and coworkers [53, 65, 66] have tested the validity of Alstrup's model. They found that the rate of carbon filament growth using an α -iron catalyst was linearly proportional to the gas-phase carbon activity at lower a_c ($a_c = K_p P_{\text{CH}_4}/P_{\text{H}_2}^2$, K_p is the equilibrium constant for reaction (3.1)). At higher a_c , the rate then became nearly independent of the gas-phase carbon activity. This is consistent with Alstrup's model, which implies that there will be a certain minimum gas-phase carbon activity necessary for the formation of the thin carbide. Below this minimum, the gas phase will pseudo-equilibrate directly with the metal. Since the carbon activity on the other side of the metal remains about unity, the rate of filament growth will increase linearly with the gas-phase carbon activity. Above this minimum, the rate will become independent of the gas-phase carbon activity because the activity of carbon dissolved in the metal is also fixed now at

the interface with the carbide. For γ -iron and nickel, however, they found that the rate did not show two regions of linear behavior, but instead a smooth transition from low a_c where the rate was strongly dependent on, to high a_c where it was nearly independent of, the gas-phase activity. Accordingly, they concluded that the presence of a surface carbide is not necessary. Rather, they noted that the diffusion coefficient and the mass fraction of carbon in the metal depend upon the carbon activity. That is, as the gas-phase activity increases without boundaries, the mass fraction of dissolved carbon stabilizes at a constant value.

From the above discussion, we can see that the general features of the mechanism of filamentous carbon formation are understood; only the driving force for the diffusion of carbon through bulk metal particles is still debated. Further understanding of the mechanism may come from experimental observation of the filament growth process, especially at the two interfaces, i.e., gas/metal interface and metal/filament interfaces. The metal particles at the two interfaces belong to different crystal orientations (planes) [46, 52]. High resolution electron microscopy (HREM) [67, 68] and in-situ electron microscopy (CAEM) [69] are being used to study these interfacial phenomena. Important clues may also come from the understanding of the chemistry leading to the surface carbon atoms, which has been missing, probably due to the lack of appropriate techniques to study surface reactions. These surface reactions must be important, as is reflected, e.g., by the observations that H_2 often plays a crucial role in the formation of filamentous carbon. On the other hand, these reactions are very complicated. Even for the simplest precursor CH_4 , there are probably many intermediates, such as CH_3 , CH_2 , and CH , before it finally decomposes to carbon atoms [53, 70]. A complete picture may only be obtained after the stoichiometry, thermodynamics, and kinetics of the process have been understood and microstructures of the carbon filament have been fully resolved.

2. Mechanism of Graphitic and Amorphous Carbon Formation. Usually, filamentous carbon coexists with two other types of carbon, i.e., laminar graphitic carbon (platelets) [40, 71-76] and amorphous carbon [38-40, 48, 77]. Laminar graphitic carbon has a structure close to that of ideal graphite; its basal plane orients almost parallel to the deposition surface. In addition, this carbon is usually featureless except that sometimes there is a polygonal network of ridges that cover the deposit surface [78-81]. These ridges are believed to form because of the differential contraction in the film on cooling [72]. For amorphous carbon, there is only two-dimensional orientation, and hydrogen is usually included in the deposit.

Laminar Graphitic Carbon (Flake, Platelet): Generally, there are two mechanisms proposed to account for the formation of this laminar graphitic carbon:

surface diffusion of carbon atoms and solution-precipitation of carbon to/from the metal. Presland and Walker [72] suggested a surface diffusion model for pyrolysis of acetylene over Ni and Pt foils at 1000 °C. They considered the solubility of carbon in both metals and concluded that the back diffusion (precipitation) of the carbon to the surface would be too quick to allow the formation of well-ordered crystalline graphite. A surface diffusion mechanism was also assumed in Baker's study for the same system (C_2H_2/Ni) [40]. Moreover, Baird later [76, 82] measured the apparent activation energy for the formation of laminar graphitic carbon as 16 kcal/mol in C_3H_6/Ni system, thereby strengthening the proposition that the formation of laminar graphitic carbon involves a surface diffusion mechanism. The value of 16 kcal/mol is intermediate between that mentioned by Derbyshire and Trimm [75] (20 kcal/mole) and the value of 6.9 ± 0.6 kcal/mol found by Mojica and Levenson [83] for the surface diffusion of carbon atoms. In contrast, Derbyshire *et al.* [75, 84, 85] showed evidence indicating that the formation of laminar graphitic carbon involved the dissolution of carbon in cobalt and nickel, followed by precipitation of the carbon as well-ordered graphite. Amorphous carbon and hydrocarbons such as CH_4 and C_2H_2 were used as the carbon source. It was shown that the nature of the carbon source was unimportant to the process. The thickness of the film was found to be limited by the solubility of carbon in nickel at any given temperature, which is quantitatively consistent with the dissolution-precipitation mechanism. Studies using in-situ hot stage SEM by Brown and Hill [80, 81, 86] confirmed that laminar graphitic carbon only occurred after the saturation solubility of carbon in the metal had been exceeded. However they also found that structural changes continued for several hours after a precipitate had appeared. Carbon-covered zones spread laterally into carbon-free areas. Perhaps both surface diffusion and solution-precipitation are involved in the formation of laminar graphitic carbon.

Amorphous Carbon (Polycrystalline, Non-Oriented): The mechanism for the formation of amorphous carbon is the least understood among the catalytic carbon deposits. Since a significant amount of hydrogen is present in the deposit, it is likely that condensation and polymerization reactions play a major role in its formation. McCarty *et al.* [38] stated that the mechanism is slow polymerization of CH_x radicals on Ni (or metal) surfaces. This is probably true because the amount of amorphous carbon formed is related to the relative amount of H_2 in the system. The higher the H_2 , the smaller the amount of amorphous carbon formed [87].

3. The Dynamics of Catalytic Carbon Formation. Catalytic carbon deposit formation is a dynamic process. The three types of catalytic deposits discussed above compete each other in a catalytic reacting system [48]. In addition, many other

morphologies, such as metal carbide, columnar [76, 82], monticular, and particulate carbons have been observed [80, 81, 88]. Moreover, filamentous carbon has been grown either on supported catalyst particles or bulk metals. What is the relationship between these different forms of deposit and the general three types? How is a bulk metal surface broken up into small particles required to sustain the formation of filamentous carbon? Some of the answers to these questions were provided by Brown and Hill using an in-situ SEM technique [80, 81, 86] in a CH_4/Fe foil system.

The carbon uptake on a metal surface usually follows a sigmoidal curve as a function of time, typical of an autocatalytic reaction. Initially carbon dissolves in the metal until the saturation solubility has been exceeded. This step is observed as an induction period. Laminar graphitic carbon films form first on a metal surface regardless of the underlying metal structure upon precipitation. Monticular carbon then develops in some area of the surface due to the changes of the underlying metal structure. The growth rate remains low up till this stage. After the lateral growth of the mounds has ceased, two kinds of particulate deposits, i.e. (i) faceted carbide crystals typically 5 mm across, and (ii) carbon encapsulated metal particles typically ≤ 1 mm diameter, are observed at the edges of the mound. The overall cluster size increases because of the creation of new particles. Each particle has growth sites for a limited number of new particles, and therefore the number in the cluster increases exponentially. As the cluster grows, the average particle size decreases, and in this way, particles of a size able to support carbon filament growth eventually develop. This particulate carbon leads eventually to the complete breakdown of the metal structure. Most of the carbon deposits are formed during this period as increasing amounts of active catalyst become available (particulate and filamentous carbon formation). The reaction finally slows down either by the formation of inert products or by encapsulation of active metal particles in the carbon deposit.

Mechanisms of Non-Catalytic Carbon Formation

Non-catalytic carbons are formed in both the pyrolysis of gas-, liquid-, or solid-phase hydrocarbons and the combustion of these hydrocarbons. Here we will only emphasize the mechanisms of gas-phase pyrolytic carbon formation.

The pyrolytic carbon formation has been reviewed by several authors [89-93]. It is known that there are two distinct forms of carbon in the pyrolysis of hydrocarbon: soft, black, and powdery carbon, which is formed in the gas phase; and hard, shiny, and vitreous carbon formed on the surface. Gas-phase carbon is usually in spherical particles consisting of small crystallites which tend to link together in a chain-like structure.

Surface carbons, on the other hand, have bigger crystallites, lower interlayer spacings, and higher densities. They are obtained as films with well-ordered crystallites.

Mechanisms proposed for the formation of these two carbons fall essentially into two categories: (i) formation of precursors via condensation and polymerization, vapor-phase nucleation and growth of large molecules, which may subsequently diffuse to the surface where they undergo dehydrogenation and incorporation into the growing carbon mass, and (ii) nucleation and growth on the surface by direct deposition of the original hydrocarbon, or a simple decomposition product thereof, or large planar molecules.

In the following subsections, terms "gas-born carbon" and "surface carbon" will be used because they directly reflect the mechanism of deposit formation, and therefore are more specific than the vague terms such as carbon black, soot, or pyrocarbon.

1. The Mechanism of Gas-Born Carbon Formation. It is expected that the process of gas-born carbon formation, which begins with relatively low molecular weight hydrocarbons and ends with huge planar "molecules" containing hundreds or thousands of carbon atoms, must involve dehydrogenation, nucleation, and growth processes. Various mechanisms differ only because of the uncertainties in the identification of essential intermediates (precursors), the ways these precursors nucleate, and their growth patterns.

Precursor of the gas-born carbon nuclei: Precursors to the carbon nuclei can possibly be formed via two routes [89, 92]. 1) Hydrocarbons polymerize, directly or after breakdown into smaller fragments, leading to unsaturated aliphatic or aromatic molecules, and finally to the PAHs. 2) Hydrocarbons lose their hydrogen atoms and yield what could be considered as the element carbon in vapor form. It is generally believed that PAHs are the precursors to the gas-born carbon.

How the PAHs form is controversial. Evidence shows that both diene mechanism (Diels-Alder reactions) and radical mechanism are possible [1]:

(a). Diels-Alder reactions

(b). Radical pyrocondensation

Generally, the distribution of primary pyrolysis products from alkanes depends on the competition of H-abstraction and β -scission reactions [94]. Radical reactions or Diels-Alder reactions lead to the formation of aromatics or alkylated aromatics. Unsubstituted aromatics react by chemical condensation to form polynuclear aromatics. Alkyl-substituted aromatics are more reactive than unsubstituted ones, the effect being more pronounced the greater the number and the length of the alkyl groups. The highest reactivity is exhibited by aromatics containing a five-membered ring system. At relatively high temperatures, the acetylene theory, which describes the formation of carbon particles from acetylene by simultaneous polymerization and dehydrogenation, is more attractive. Frenklach [95] has proposed a general mechanism of PAH and soot formation shown as Figure 18. Glassman [96] combined the results from Frenklach *et al.*, Kern *et al.* [97], and Colket's work [98] and proposed a generalized mechanism for PAH formation (see Figure 19). He claims that this generalized mechanism describes the overall soot formation paths for practically every fuel studied to that date and hold for both premixed and diffusion flame systems, as well as shock tube pyrolysis experiments.

Nucleation and growth: In contrast to soot formation, homogeneous nucleation is believed to be the major nucleation scheme in the gas-born carbon formation [92]. The formation of gas-born carbon particles can be viewed as a phase change from a gas to a condensed state. The question which arises is concerned with the physical state of the nuclei: are they liquid or solid?

The concept that involves the liquid nuclei is generally favored [99-102]. It was considered that the particles were liquid when they were deposited, and the term "droplets" was used to describe the particles. In addition, the flow of these droplets subsequent to deposition was believed [101, 102] to be responsible for some of the variations in structure under different deposition conditions. A liquid-based deposition mechanism has also been proposed by Je and Le [103] to explain microstructural changes induced in pyrolytic carbons by changes in deposition temperature.

The early concept involving solid nuclei has not been popular because first, it considered the gas-born carbon formation in terms of condensation of carbon vapor, and second, it seems difficult to imagine the reorganization of individual crystallites of these solid nuclei in large concentric carbon layers. In fact, Lahaye and Prado wrote in 1979: "There is no longer any doubt that nuclei are the result of a gas-liquid phase change. The nuclei are liquid microdroplets whose shape is in the geometric form of the final particle." However, Kaae [104] proposed a mechanism involving solid particles formed in the gas phase in the pyrolysis of propylene below 1700 °C. It was observed that there were small growth cones within the larger growth features, and these sub-growth feature cones were extended in the macroscopic growth direction. Kaae found no evidence for the incorporation of liquid droplets in the deposits even at the lowest practical temperature (1300 °C) and concluded that the growth features are formed in the solid state. The macroscopic anisotropy was formed by a deposition process rather than by a flow of droplets, as previously suggested.

An agglomerate model was proposed [102] to specifically account for the particle growth in the gas phase. In short, nuclei formed in the gas phase grow to sub-agglomerates and to agglomerates by the accumulation of molecules, molecule fragments, or other nuclei, and then the agglomerate deposits on the substrate. The orientation of the pyrolytic carbon is decided by the viscosity and the sphericity of the agglomerate. The growth after deposition will be discussed together with the surface carbon growth in the following subsection.

2. The Mechanism of Surface Carbon Formation. Surface carbon formation has been studied considerably less than gas-born carbon because of a lack of experimental methods for studying elemental processes on solid surfaces. For comparison, a similar approach to the gas-born carbon is still adapted to describe the surface carbon formation in terms of precursor formation, nucleation, and growth.

Precursor to the surface carbon: Precursors to the surface carbon are not as certain in the case of gas-born carbon. Palmer [105] assumed that species which were able to induce the formation of gas-born carbon could also lead to the formation of

surface carbon. The sequence for carbon formation from a pyrolyzing hydrocarbon may be divided into four stages:

Stage I	Gaseous decomposition condensation reactions, polymerization	⇒	Deposition
Stage II	Formation of polyacetylenes and related species, nucleation	⇒	Deposition
Stage III	Growth of nuclei, decomposition of gases on particle surfaces	⇒	Deposition
Stage IV	Agglomeration, curing of particles casting off of residual species	⇒	Deposition

This scheme indicates the possibility that deposits on surfaces may be formed at any stage in the process. The precursors to the surface carbon, referring to stages I and II, range from very small species such as hydrocarbon radicals to polymeric intermediates, which are large molecules or radicals. These species can orient themselves well on the surface and produce a relatively well-ordered anisotropic deposit.

Tesner and colleagues have long advocated a theory of direct decomposition of the original hydrocarbons on growing carbon surfaces [106]. In a comprehensive kinetic study of surface carbon formation, Tesner [93] found that the greatest value of activation energy of nucleation for methane was 76 kcal/mol, which is smaller than the activation energy of the detachment of one (102 kcal/mol) or two (90 kcal/mol) hydrogen atoms from methane molecule to form $\text{CH}_3\cdot$ or $\text{CH}_2\cdot\cdot$ radicals. For all the other hydrocarbons, the activation energy of nucleation is much less than for methane. Tesner concluded that the formation of radicals from hydrocarbons in the gas phase is not a limiting stage of surface carbon formation, and both processes, the nucleation and growth of crystallites, originate from stable molecules of the initial hydrocarbon.

Carroll and Murphy [107, 108], from analysis of the effluent gases, concluded that ethane rapidly formed a near-equilibrium mixture of ethane, ethylene, and acetylene during pyrolysis in a flow system between 900 and 1000 K, and that acetylene was the source of the carbon deposit. A recent study on acetylene by the same authors [109] showed that carbon and ethylene formation were isolated from acetylene consumption, which is consistent with a process involving surface saturation. The mechanism they

proposed involves a slow reaction at active sites, by which acetylene is chemically adsorbed as surface species serving as the common source of carbon, ethylene, and other pyrolysis products.

The possibly more diverse choices of precursors to the surface carbon than to the gas-born carbon may further lie in the differences in the nucleation and growth processes between these two forms of carbons.

Nucleation and growth of surface carbon: Surface carbon is a laminated structure built up of approximately parallel blocks of graphite hexagonal layers. The molecular mechanism of nucleation and growth of crystallites are far from understood. Only indications of the molecular mechanism can be deduced. Tesner's [93] kinetic study showed that the rate of the topochemical process of surface carbon formation, as well as the nucleation and growth of crystallites, could be expressed as first-order heterogeneous processes, and the temperature dependence of the overall rate could be expressed by the Arrhenius equation over a broad temperature range. This indicates that both the nucleation and growth of crystallites are chemical processes. In addition, it was suggested [104] that depositing molecules react with molecules on a surface in a preferred way to produce order between one crystallite and the next. The structural variations at different temperatures can be explained by changes in the reactivity of the depositing molecular species.

Nucleation and growth are most likely initiated at active sites of the surface. When all the growth cones in a deposit originate on the substrate, the structure is called "singularly" nucleated; when new grains are nucleated throughout the deposit, the structure is called "regenerative" or "continuously" nucleated [90]. An example of a growth cone caused by an isolated substrate asperity is shown in Figure 20(a) [110]. When conditions are adjusted such that gas-born carbon forms and grows, regenerative structures are deposited. Coffin [110] has demonstrated how the attachment of a gas-born particle to the growing surface of a deposit provides a genetic protrusion from which a new growth can be formed (see Figure 20(b)).

Since non-catalytic deposits collected on the surface may come from gas-born carbon and surface carbon, their morphologies will depend on the relative importance of these two processes [90]. The deposition of surface carbon results in a decrease of surface area, thus reducing the formation of anisotropic surface carbon. Meanwhile, more finely divided gas-born carbon is formed in the gas phase and incorporated on to the surface of the formerly deposited carbon; consequently the surface area temporarily increases, and the conditions for the formation of a new layer of surface carbon are reestablished. This can also occur, although to a lesser extent, for the formation of a surface carbon on gas-

born carbon particles [92]. The competition between gas-born and surface carbon could give the deposit a distinctly layered-structure.

3. Carbon Formation from Heavy Oils. If we understand the carbon formation from both ends, i.e., light and heavy hydrocarbons, it might be easier to understand deposit formation from intermediate hydrocarbons such as jet fuels.

There are generally three kinds of coke deposit formed on catalysts [111] and on metal foils [112] from heavy oils : (i) metal carbide; (ii) precipitated asphaltenes or tars; (iii) mesophase coke. Asphaltenes contained in the heavy oils have been identified as the major source for each of the deposits. Crystal-like nickel carbide grains with irregular or needle-shapes were seen on nickel foils but not on stainless steel foils when heavy oils in a tubing bomb were thermally stressed between 445–550 °C [112]. The structure of this deposit varies with the feed but does not vary much with the reaction conditions. On the surface of catalysts, adsorption of asphaltenes on acidic sites is mainly responsible for the initial coke deposition. The preferred adsorption is because of the interaction between basic nitrogen containing groups in the asphaltenes and acidic sites on the catalyst [111]. Mesophase coke is formed probably by condensation reactions involving asphaltenes. The mechanisms of mesophase development have been reviewed [113, 114] thus will not be discussed any further.

Comparisons of Catalytic and Non-Catalytic Carbon Formation

Having discussed the mechanisms of each kind of carbon deposit formation independently, we are now ready to look the processes of deposit formation as a whole. In practice, pyrolysis or thermal stressing of hydrocarbons takes place in metal-walled reactors. Conditions for catalytic and non-catalytic carbon formations are all satisfied for a new reactor (or a new/regenerated catalyst). As deposit builds up, the initial metal surface is gradually replaced by a carbon deposit surface; only non-catalytic carbon deposit would then be expected to form. However, catalytic carbon formation plays an important role for a long time. This is probably because (i) the induction time required for carbon formation prevents the upstream of the tube from being covered for a long time and thus influences the downstream reactions; (ii) the carburization and the subsequent disruption of the reactor wall cause a "catalytic effect" [39].

Albright and Marek [115-117] have observed catalytic (filamentous) and non-catalytic (gas-born and surface) carbon formation on stainless-steel (Incoloy 800) surface in pyrolyzing hydrocarbons (C_2H_2 , C_2H_6 , C_3H_8 , $C_6H_5CH_3$) to ethylene and various olefins. The rate of total deposit formation (r_c) can be expressed as

$$r_c = \frac{dy}{dt} = a + bce^{-ct} \quad \text{or}$$

$$y = at + b(1 - e^{-ct})$$

where a is the rate of formation of non-catalytic deposit, bc is the initial rate of formation of catalytic (filamentous) deposit, c is the decay constant for catalytic deposit, and y is the amount of deposit on the surface at run time t . Initially, filamentous carbon formation is dominant. Later, at low or intermediate residence time, gas-born carbon formation is dominant. At high temperatures, surface carbon formation becomes dominant and is responsible for the uniform growth of filament size and spherical deposit. A cross-section of the deposit morphology is schematically shown as Figure 21. It is noteworthy that some of the non-catalytic surfaces they listed are quartz, aluminized stainless-steel, silicized steels, and steels coated with manganese-rich surfaces.

Besides the unique appearance of filamentous carbon and the fact that it usually contains 1–2 wt % of metal, different forms of carbon may be distinguished by their crystalline structure and the C/H elemental analysis. Such information is given in Table 3 [39].

Conclusions

An overview of catalytic and non-catalytic carbonaceous deposit formation from thermal stressing of hydrocarbons is schematically shown in Figure 22.

Autoxidation and pyrolysis of jet fuels under thermal stressing can lead to the formation of carbonaceous deposits. The mechanisms of deposit formation are relatively well documented from the autoxidation of jet fuels, but are far from understood from their pyrolysis. Free radical decomposition, polymerization, condensation reactions produce PAHs which nucleate and grow to form carbonaceous deposit under pyrolysis conditions. Liquid mesophase development is also involved in the deposit formation. The role of a metal surface in deposit formation is uncertain. A copper surface may accelerate the deposit formation under autoxidation conditions. However, there are no systematic studies of the possible catalytic effects of metal surfaces on deposit formation under pyrolysis conditions.

Catalytic carbon deposits from pyrolysis of light hydrocarbons include filamentous, laminar graphitic, and amorphous carbons. Filamentous carbon forms via the bulk diffusion of elemental carbon atoms through the metal particles. The driving force for this diffusion process is still debated. It is likely that a metastable metal carbide helps to establish the concentration gradient from the leading to the trailing face of the metal particle. For the formation of laminar graphitic deposit, both dissolution-precipitation and

surface diffusion are probably part of the mechanisms. Finally, amorphous carbon may form through the polymerization of small hydrocarbon species.

Non-catalytic pyrolytic carbons come from two sources: gas-born carbon and surface carbon. Precursors to these two distinct forms of carbon, nucleation of the precursors, as well as the growth pattern may all be different. The precursors to the former probably are PAHs; homogeneous nucleation and agglomeration have been suggested as its nucleation and growth mechanisms. In terms of surface carbon formation, the precursors are probably more diverse, and nucleation and growth processes can be better described as chemical in nature. During the carbonization of heavy hydrocarbons, liquid phase mesophase carbon and precipitated tars are found to be the predominant carbon deposits.

Studies of the deposit formation from jet fuel pyrolysis have explored a new field in the spectrum of carbon formation from hydrocarbon pyrolysis. These studies are thus of great importance not only because of their practical applications, but also because of their potential power to gain new insights into various carbon formation processes.

References

1. E. Fitzer, K. Mueller and W. Schaefer, in *The Chemistry and Physics of Carbon*, P. L. Walker Jr., Editor. Dekker: New York, 237-383 (1971).
2. L. E. Faith, G. H. Ackerman, H. T. Henderson, A. W. Ritchie and L. B. Ryland, *Hydrocarbon Fuels for Advanced Systems*. Aero Propulsion Laboratory: AFAPL-TR-70-71, Part III (1972).
3. P. H. Taylor and W. A. Rubey, *Energy & Fuels*, **2**(6), 723-728 (1988).
4. *CRC Literature Survey on the Thermal Oxidation Stability of Jet Fuel*. Coordinating Research Council, Inc., Atlanta, Georgia: CRC Report No. 509 (1979).
5. W. F. Taylor and T. J. Wallace, *Ind. Eng. Chem., Prod. Res. Dev.*, **6**, 258-262 (1967).
6. W. F. Taylor, *I & EC Prod. Res. Dev.*, **8**(4), 375-380 (1969).
7. B. M. Fabuss, R. Kafesjian, J. O. Smith and C. N. Satterfield, *I & EC Proc. Des. Dev.*, **3**(3), 248-254 (1964).
8. W. F. Taylor, *Ind. Eng. Chem., Prod. Res. Dev.*, **13**(2), 133-138 (1974).
9. R. N. Hazlett, J. M. Hall and M. Matson, *Ind. Eng. Chem., Prod. Res. Dev.*, **16**(2), 171-177 (1977).

10. R. N. Hazlett, in *Frontiers of Free Radical Chemistry*, W. A. Pryor, Editor. Academic Press: New York, 195-223 (1980).
11. J. W. Frankenfeld and W. F. Taylor, *Ind. Eng. Chem. Prod. Res. Dev.*, **19**(1), 65-70 (1980).
12. R. Roback, E. J. Szetela and L. J. Spadaccini, *J Eng. Gas Turbines & Power*, **105**, 59-65 (1983).
13. W. S. Kim and D. A. Bittker, *Liquid Phase Products and Solid Deposit Formation From Thermally Stressed Model Jet Fuels*. NASA Lewis Research Center: NASA-TM 86874 (1984).
14. R. T. Reddy and N. P. Cernansky, *Energy & Fuels*, **2**(2), 205-213 (1988).
15. R. M. Schirmer, *SAE* paper 700258 (1970).
16. C. Song, Y. Peng, H. Jiang and H. H. Schobert, in *Symposium on Structure of Jet Fuels III*, Div. Petroleum Chem. San Francisco, ACS, **37**, 484-492 (1992).
17. S. Eser, C. Song, K. Gergova, M. Parzynski and Y. Peng, in *Symposium on Structure of Jet Fuels III*, Div. Petroleum Chem. San Francisco, ACS, **37**, 463-468(1992).
18. J. D. Smith, *Aircraft Eng.*, **39**, 19-22 (1967).
19. W. F. Taylor, *J Appl. Chem.*, **18**, 251-254 (1968).
20. W. F. Taylor, *J Appl. Chem.*, **19**, 222-226 (1969).
21. E. L. Wong and D. A. Bittker, *Effect of Hydrocarbon Fuel Type on Fuel Thermal Stability*. NASA: NASA-TM 82916 (1982).
22. C. E. Baker, D. A. Bittker, S. W. Cohen and G. T. Seng. *AGARD Conference Proceedings No. 353, Combustion Problems in Turbine Engines*. 2-1 - 2-10 (1983).
23. D. R. Kendall and J. S. Mills, *Proceedings of the Aerospace Technology Conference and Exposition*. Long Beach, CA: 143 (1985).
24. L. B. Hazell, C. Baker, P. David and A. D. Fackerell, *Surface and Interface Analysis*, **9**, 507-513 (1986).
25. C. Baker, P. David, R. Finney, D. Hall and R. Swatridge, *200th ACS meeting, Div. of Fuel*, ACS, **35**, 1233-1246 (1990).
26. L. L. Stavinoha, D. W. Naegeli and L. McInnis. *200th ACS Meeting, Div. of Fuel*, ACS, **35**, 1315-1323 (1990).
27. J. S. Chin, A. H. Lefebvre and F. T. Y. Sun, *J Eng. Gas Turbines & Power*, **114**, 353-358 (1992).
28. J. S. Chin and A. H. Lefebvre, *J. Prop. Power*, **8**(6), 1152-1156 (1992).

29. J. TeVelde, L. J. Spadaccini, E. J. Szetela and M. R. Glickstein, *Combustion Problems in Turbine Engines Held at the Propulsion and Energetics Panel Symposium (62nd Cesme (Turkey))*. United Technologies Research Center, East Hartford, CT (1983).
30. A. J. Giovanetti and E. J. Szetela, *J Propulsion*, **2**(5), 450-456 (1986).
31. P. J. Marteney and L. J. Spadaccini, *J Eng. Gas Turbines & Power*, **108**, 648-653 (1986).
32. L. S. Lobo and D. L. Trimm, *Nature phys. sci.*, **234**(11), 15-16 (1971).
33. J. Rostrup-Nielsen, *J Catalysis*, **48**, 155-165 (1977).
34. A. Oberlin, M. Endo and T. Koyama, *J Crystal Growth*, **32**, 335-349 (1976).
35. G. G. Tibbetts, M. G. Devour and E. J. Rodda, *Carbon*, **25**(3), 367-375 (1987).
36. M. Ishioka, T. Okada, K. Matsubara and M. Endo, *Carbon*, **30**(6), 865-868 (1992).
37. M. Ishioka, T. Okada, K. Matsubara and M. Endo, *Carbon*, **30**(6), 859-863 (1992).
38. J. G. McCarty, P. Y. Hou, D. Sheridan and H. Wise, in *Coke Formation on Metal Surfaces*, L. F. Albright and R. T. K. Baker, Editors. Americal Chemical Society: Washington, D. C., 253-282 (1982).
39. D. L. Trimm, in *Pyrolysis: Theory and Industrial Practice*, L. F. Albright, B. L. Crynes and W. H. Corcoran, Editors. Academic Press: New York, 203-232 (1983).
40. R. T. K. Baker, M. A. Barber, P. S. Harris, F. S. Feates and R. J. Waite, *J Catalysis*, **26**, 51-62 (1972).
41. J. R. Rostrup-Nielsen, *J Catalysis*, **27**, 343-356 (1972).
42. R. T. K. Baker, P. S. Harris, R. B. Thomas and R. J. Waite, *J Catalysis*, **30**, 86-95 (1973).
43. C. A. Bernardo and L. S. Lobo, *J Catalysis*, **37**, 267 (1975).
44. R. T. K. Baker and P. S. Harris, in *Chemistry and Physics of Carbon*, P. L. Walker Jr. and P. A. Thrower, Editors. Dekker: New York, 83-165 (1978).
45. E. Boellaard, P. K. de Bokx, A. J. H. M. Kock and J. W. Geus, *J Catalysis*, **96**, 481-490 (1985).
46. I. Alstrup, *J Catalysis*, **109**, 241-251 (1988).
47. R. T. K. Baker and R. J. Waite, *J Catal.*, **37**, 101 (1975).
48. R. T. K. Baker, D. J. C. Yates and J. A. Dumesic, in *Coke Formation on Metal Surfaces*, L. F. Albright and R. T. K. Baker, Editors. Americal Chemical Society: Washington, D. C., 1-21 (1982).
49. D. L. Trimm, *Catal. Rev. - Sci. Eng.*, **16**(2), 155-189 (1977).
50. R. T. K. Baker, J. R. Alonzo, J. A. Dumesic and D. J. C. Yates, *J Catalysis*, **77**, 74-84 (1982).

51. W. L. Holstein and M. Boudart, *Lat. Am. J Chem. Eng. Appl. Chem.*, **13**, 107-120 (1983).
52. R. T. Yang and J. P. Chen, *J Catalysis*, **115**, 52-64 (1989).
53. E. C. Bianchini and C. R. F. Lund, *J Catalysis*, **117**, 455-466 (1989).
54. J. J. Lander, H. E. Kern and A. L. Beach, *J Appl. Phys.*, **23**, 1305 (1952).
55. T. Wada, H. Wada, J. F. Elliott and J. Chipman, *Metal Trans.*, **4**, 2199 (1971).
56. M. Eizenberg and J. M. Blakely, *J Chem. Phys.*, **71**(8), 3467-3477 (1979).
57. M. Eizenberg and J. M. Blakely, *Surface Science*, **82**, 228-236 (1979).
58. M. P. Manning and R. C. Reid, *Ind. Eng. Chem., Proc. Des. Dev.*, **16**(3), 358-361 (1977).
59. M. P. Manning, J. E. Garmirian and R. C. Reid, *Ind. Eng. Chem. Proc. Des. Dev.*, **21**, 404-409 (1982).
60. P. K. de Bokx, A. J. H. M. Kock, E. Boellaard, W. Klop and J. W. Geus, *J Catalysis*, **96**, 454-467 (1985).
61. G. G. Tibbetts, *J Crystal Growth*, **66**, 632-638 (1984).
62. A. Sacco Jr. and P. Thacker, *16th Bienn. Conf. Carbon*. Univ. California, San Diego: American Chemical Society (1983).
63. A. Sacco Jr., P. Thacker, T. N. Chang and A. T. S. Chiang, *J Catalysis*, **85**, 224-236 (1984).
64. A. J. H. M. Kock, P. K. de Bokx, E. Boellaard, W. Klop and J. W. Geus, *J Catalysis*, **96**, 468-480 (1985).
65. S. A. Safvi, E. C. Bianchini and C. R. F. Lund, *Carbon*, **29**(8), 1245-1250 (1991).
66. P. Chitrapu, C. R. F. Lund and J. A. Tsamopoulos, *Carbon*, **30**(2), 285-293 (1992).
67. D. J. Smith, M. R. McCarney, E. Tracz and T. Borowiecki, *Ultramicroscopy*, **34**, 54-59 (1990).
68. E. Tracz, R. Scholz and T. Borowiecki, *Appl. Catalysis*, **66**, 133-148 (1990).
69. M. S. Kim, N. M. Rodriguez and R. T. K. Baker, *J Catalysis*, **134**, 253-268 (1992).
70. S. T. Ceyer, *Langmuir*, **6**, 82-87 (1990).
71. A. E. Karu and M. Beer, *J Appl. Phys.*, **37**, 2179 (1966).
72. A. E. B. Presland and P. L. Walker Jr., *Carbon*, **7**, 1-8 (1969).
73. S. D. Robertson, *Carbon*, **8**, 365-374 (1970).
74. S. D. Robertson, *Carbon*, **10**, 221-229 (1972).
75. F. J. Derbyshire and D. L. Trimm, *Carbon*, **13**, 189-192 (1975).
76. T. Baird, *Fuel*, **63**, 1081-1099 (1984).
77. T. Baird, J. R. Fryer and B. Grant, *Carbon*, **12**, 591-602 (1974).

78. A. E. B. Presland, C. Roscoe and P. L. Walker Jr. *3rd Conference on Industrial Carbons and Graphite*. London: Society of Chemical Industry, London. 116-120 (1970).
79. G. Blau and A. E. B. Presland, *3rd Conference on Industrial Carbons and Graphite*. London: Society of Chemical Industry, London. 121-125 (1970)
80. A. M. Brown and M. P. Hill, in *Coke Formation on Metal Surfaces*, L. F. Albright and R. T. K. Baker, Editors. American Chemical Society: Washington, D. C., 193-222 (1982).
81. A. M. Brown and M. P. Hill, *J Microscopy*, **153**, 63-74 (1989).
82. T. Baird, *Carbon*, **15**, 379-382 (1977).
83. J. F. Mojica and L. L. Levenson, *Surface Science*, **59**, 447-460 (1976).
84. F. J. Derbyshire, A. E. B. Presland and D. L. Trimm, *Carbon*, **10**, 114 (1972).
85. F. J. Derbyshire, A. E. B. Presland and D. L. Trimm, *Carbon*, **13** 111-113 (1975).
86. A. M. Brown and M. P. Hill, *J Microscopy*, **153**, 51-62 (1989).
87. G. A. Jablonski, F. W. Geurts, A. Sacco Jr. and R. R. Biederman, *Carbon*, **30**(1), 87-98 (1992).
88. M. Audier, J. Guinot, M. Coulon and L. Bonnetain, *Carbon*, **19**, 99-105 (1981).
89. H. B. Palmer and C. F. Cullis, in *Chemistry and Physics of Carbon*, P. L. Walker Jr., Editor. Dekker: New York, 265-325 (1965).
90. J. C. Bokros, in *Chemistry and Physics Carbon*, P. L. Walker Jr., Editor. Dekker: New York, 1-118 (1969).
91. W. V. Kotlensky, in *Chemistry and Physics of Carbon*, P. L. Walker Jr., Editor. Dekker: New York, 176 (1973).
92. J. Lahaye and G. Prado, in *Chemistry and Physics of Carbon*, P. L. Walker Jr. and P. A. Thrower, Editors. Dekker: New York, 168-294 (1978).
93. P. A. Tesner, in *Chemistry and Physics of Carbon*, P. L. Walker Jr. and P. A. Thrower, Editors. Dekker: New York, (1985).
94. M. L. Poutsma, *Energy & Fuels*, **4**(2), 113-131 (1990).
95. M. Frenklach, D. Clary, W. C. Gardiner Jr. and S. E. Stein, in *Twentieth Symposium (International) on Combustion*. The Combustion Institute, 887-901 (1985).
96. I. Glassman, in *Soot Formation in Combustion, An International Round Table Discussion*, H. Jander and H. G. Wagner, Editors. Gottingen, 67-119 (1989).
97. R. D. Kern, C. H. Wu, J. N. Young, K. M. Pamedemukkala and S. H. J., *Energy & Fuels*, **2**, 454 (1988).
98. M. B. I. Colket, in *Twenty-First Symposium (International) on Combustion*. Pittsburgh: The Combustion Institute, 851 (1988).

99. J. C. Bokros, *Carbon*, **3**, 17-29 (1965).
100. J. Lahaye, G. Prado and J. B. Donnet, *Carbon*, **12**, 27 (1974).
101. L. H. Ford and C. F. Bilsby, *J Nucl. Mat.*, **60**, 79-88 (1976).
102. J. Linke, K. Koizlik and H. Nickel, *Nucl. Tech.*, **35**, 257-262 (1977).
103. J. H. Je and J. Y. Lee, *Carbon*, **22**(6), 563-570 (1984).
104. J. L. Kaae, *Carbon*, **23**(6), 665-673 (1985).
105. H. B. Palmer, *J Chim. Phys.*, April (special issue), 87 (1969).
106. P. A. Tesner, in *7th Symposium on Combustion*. Butterworths, London, Oxford (1959).
107. R. W. Carroll and D. B. Murphy, in *16th Biennial Conference on Carbon, Extended Abstract and Program*, 114 (1983).
108. D. B. Murphy and R. W. Carroll, in *19th Biennial Conference on Carbon, Extended Abstract and Program*, 446 (1989).
109. D. B. Murphy and R. W. Carroll, *Carbon*, **30**(1), 47-54 (1992).
110. L. F. Coffin Jr., *J Ameri. Ceramic Soc.*, **47**(10), 473-478 (1964).
111. M. Absi-Halabi, A. Stanislaus and D. L. Trimm, *Appl. Catal.*, **72**, 193-215 (1991).
112. E. A. Blekkan and A. Holmen, *Carbon*, **25**(6), 827-835 (1987).
113. J. D. Brooks and G. H. Taylor, in *Chemistry and Physics of Carbon*, P. L. Walker Jr., Editor. Dekker: New York, 243-285 (1968).
114. H. Marsh and R. Menendez, in *Introduction to Carbon Science*, H. Marsh, Editor. 37-73 (1989).
115. L. F. Albright and J. C. Marek, *Ind. Eng. Chem. Res.*, **27**(5), 743-751 (1988).
116. L. F. Albright and J. C. Marek, *Ind. Eng. Chem. Res.*, **27**(5), 751-755 (1988).
117. L. F. Albright and J. C. Marek, *Ind. Eng. Chem. Res.*, **27**(5), 755-759 (1988).

Task 4. Coal-based Fuel Stabilization Studies

1. Thermal Stability studies Using the Model Compound Dodecane (Contributed by Leena Selvaraj, Michael M. Coleman, and Chunshan Song)

Introduction

This study is a continuation of the work from the previous quarterly report. Dodecane has been used as a model compound to investigate the effect of the additive, benzyl alcohol, during pyrolysis under an atmosphere of air. The changes observed in the

yields of the major products obtained upon stressing dodecane at elevated temperatures with and without benzyl alcohol are investigated as a function of time. The pyrolysis products of benzyl alcohol in the reaction medium are also studied. The results obtained are useful in elucidating the underlying reaction mechanisms. Deuterated dodecane has also been used to probe the hydrogen-donating character of benzyl alcohol.

Experimental

Two sets of experiments were performed; the first on pure dodecane and the second on dodecane with 5% (by volume) benzyl alcohol. Thermal stressing was performed for different times on 10 mL samples at 425°C using 15 mL type 316 stainless steel microreactors under 100 psi of air. The microreactor containing the sample was purged with 1000 psi of UHP-grade N₂ for five times 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 collect head-space gases. Because of the high cost of the deuterated compounds, only 2.5 mL of deuterated dodecane was used. The estimated percentage of deuterium in the deuterated dodecane, using GCMS analysis, was found to be 99.66.

Gas chromatographic analyses were performed to quantify the liquid products using a Hewlett Packard GC with a FID detector; the column used was Rtx-50. The temperature program used was 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 analyzed and quantified using Perkin Elmer Autosystem GC with dual detectors (FID and TCD). A Hewlett Packard GC with mass detector was used for the qualitative analysis.

Discussion

1. Pyrolysis of Dodecane with and without Benzyl Alcohol. Gas chromatographic analyses of neat dodecane and dodecane with 5 vol.% benzyl alcohol indicate that the major pyrolysis products are *n*-alkanes and 1-alkenes (< C₁₂) for short periods of time of thermal stressing (up to about six hours). However, longer periods of stressing favor higher yields of *n*-alkanes and after stressing for twelve hours 1-alkenes are barely detected. Figure 23 shows the yields of C₅ to C₁₀ *n*-alkanes on stressing dodecane with and without benzyl alcohol at 425°C under 100 psi air for 0, 1, 3, 6, and 12h. This figure shows that in the presence of benzyl alcohol the degradation of dodecane to *n*-alkanes is retarded for about 6h of stressing. The longer the duration of thermal stressing, the greater

is the cracking of dodecane into low molecular weight alkanes. It can be also seen that the abundance of paraffins ($C_5 > C_6 > C_7 > C_8 > C_9 > C_{10}$) increases in a linear fashion with the time of stressing after an initial short induction period without benzyl alcohol, but in its presence an induction period of some six hours is indicated. Figure 24 shows the yields of C_5 to C_{10} 1-alkenes on stressing dodecane with and without benzyl alcohol at 425°C under 100 psi air for 0, 1, 3, and 6h. This figure shows that benzyl alcohol also retards the formation of 1-alkenes. In contrast to alkanes, the concentration of 1-alkenes maximize between one to three hours of stressing without benzyl alcohol, and between three to six hours with benzyl alcohol. This is entirely consistent with the data obtained from the Fourier transform infrared (FTIR) spectroscopy as reported in the previous quarterly report. The disappearance of alkenes after longer stressing periods can be related to their conversions into other products by condensation, cyclization and aromatization reactions.

The total yield of gaseous hydrocarbons products upon stressing dodecane without and with 5% (by volume) benzyl alcohol is shown in Figure 25. This plot also indicates that benzyl alcohol retards the formation of gaseous hydrocarbons for about six hours of stressing. These encouraging results prompted us to follow quantitatively benzyl alcohol and its products in the reaction mixture.

2. Benzyl Alcohol Degradation in the Reaction Mixture. Figure 26 (top) shows the amount of benzyl alcohol present in dodecane upon stressing the sample at 425°C under 100 psi air for 0, 3, 6, and 12h. The benzyl alcohol is essentially completely consumed in about six hours of reaction time. Figure 26 (bottom) shows the amount of dodecane present in the sample with and without benzyl alcohol after stressing under similar reaction conditions. The dramatic effect of the presence of benzyl alcohol on the degradation of dodecane is obvious and it is evident that while a significant concentration of benzyl alcohol exists in the mixture it acts as a "sacrificial lamb" and retards the degradation of dodecane.

Figure 27 shows the amount of benzyl alcohol, benzaldehyde, dibenzylether, benzene and toluene present in the reaction mixture after stressing. In the time interval where benzyl alcohol functions as an effective additive in retarding the degradation of dodecane, the major reaction product is benzaldehyde. Based on this observation, we infer that benzyl alcohol donates hydrogen to molecular species containing free radicals that are formed in the reaction medium prior to being oxidized to benzaldehyde. On stressing for longer time, benzene and toluene are the only products observed by gas chromatographic analysis; the FTIR results reported earlier also indicate that some benzoic acid is formed, which can not be detected by GC analysis due to the limitation of

the particular column used. Benzene and toluene can be obtained via the pyrolysis of benzaldehyde and dibenzylether; while benzoic acid can be formed by simple oxidation of benzaldehyde.

3. Mechanistic Studies Using Deuterated Dodecane. Figure 28 summarizes the proposed primary reaction scheme for the thermal degradation of deuterated dodecane in the presence of benzyl alcohol. Under these reaction conditions pyrolysis of dodecane proceeds via free radical mechanisms. The first step is initiation resulting in the formation of free radical ($R\cdot$). This radical abstracts a deuterium from the deuterated dodecane molecule. At this stage the free radical either abstracts the benzylic hydrogen from benzyl alcohol and forms an alkane (m-1) or it undergoes β -scission forming a completely deuterated alkene and a free radical, which in turn can abstract hydrogen from benzyl alcohol resulting in the formation of an alkane (m-1). Deuterium can also be abstracted from the alkene, resulting in a radical, which in turn can abstract hydrogen from benzyl alcohol resulting in an alkene (m-1). These (m-1) species can further undergo the same cycle, producing (m-2) and other species.

Evidence that benzyl alcohol donates hydrogen to the reaction system in the manner depicted in Figure 28 was obtained from the following study. Deuterated dodecane (2.5 mL) without and with 5% (by volume) protonated benzyl alcohol was stressed at 425°C under 100 psi air for 3h. Figures 29 and 30 show the yields of C_6 to C_{11} *n*-alkanes, analyzed by GC/MS. In these plots, molecular ion (M) represents the completely deuterated molecule, (M-1) represents the replacement of one deuterium in the molecule by a proton, and (M-2) represents two deuteriums are replaced by two protons. Comparing Figures 29 and 30, it is evident that addition of benzyl alcohol to deuterated dodecane leads to the formation of more M-1 and M-2 species with respect to M species. (Note that in examining the data the deuterated dodecane is not 100% deuterated, and consequently there are M-1 and M-2 species in the "pure" starting material.) Figures 31 and 32 show the corresponding yields of C_6 to C_{11} 1-alkenes on stressing deuterated dodecane with and without five percent benzyl alcohol. Again we observe a similar effect. These observations are strong evidence that benzyl alcohol donates hydrogen and acts as a free radical scavenger.

2. Screening Potential Jet Fuel Stabilizers Using the Model Compound Dodecane (Contributed by Emily M. Yoon, Michael M. Coleman, Chunshan Song).

Introduction

Studies have been performed qualitatively on potential thermal stabilizers for jet fuels and are reprinted in a recent publication [1]. Classic antioxidants, coal liquefaction reagents, and some alcohols were considered. In this reporting period, quantitative studies were performed on potential stabilizers. Since the typical jet fuel is a highly complex mixture, dodecane was chosen as a model compound, as it is the most abundant hydrocarbon in jet fuels.

Experimental

The reactants used in these studies were purchased from Aldrich Chemical Co. Dodecane, tetralin, 9,10-dihydrophenanthrene, tetrahydroquinoline, and benzyl alcohol were used without further purification. A sample of Mark 1901 (alkyltin mercaptide) was obtained from Witco. Thermal stressing was performed at 450°C in 25mL type 316 stainless steel microreactors under 1.0 MPa of UHP-grade N₂. The microreactor containing the sample was purged five times with UHP-grade N₂ at 7.0 MPa to minimize the presence of dissolved oxygen and finally pressurized with 1.0 MPa of N₂. It was then placed in a preheated sand bath at 450°C for 10–40min, followed by quenching into cold water.

Quantification of the liquid products was performed by using a Hewlett Packard GC with a FID detector. The column used was Rts-50. The column temperature was programmed 40°C to 280°C at a heating rate of 4°C/min after 5 min isothermal period at 40°C, followed by 10min isothermal period at 280°C. The split mode of injection was used. For each sample, approximately 0.1 µl was injected to the column. The molar yields of the dodecane were calculated as follows:

$$\text{Molar Yield(\%)} = [(A\%_{dd} * W_{\text{liquid}})/MW_{dd}]/N_{dd}$$

where dd indicates the dodecane; A%_{dd} is the integrated area% of dodecane; W_{liquid} is the total weight of the liquid product; N_{dd} is the number of moles of reactant dodecane. Then, dodecane conversion was calculated as given:

$$\text{Dodecane conversion(mol\%)} = 100\% - \text{molar yield(\%)}$$

Results and Discussion

1.Dodecane Conversion Figure 33 represents the effects of the additives on the molar% dodecane conversion after thermally stressing for the time period of 10, 20, 30, 40 min at 450°C. Each additive was added 5% based on volume into dodecane. Without additives, the conversion of dodecane ranges from 4 to 44% between 10 to 40 min, respectively. The dodecane conversion decreases with the additives, except for the classical antioxidant Mark 1901. Black carbonaceous solids were obtained from the sample of dodecane plus 5% Mark 1901 while other samples only had liquid and gaseous products. Based on 5 vol% additives used, tetrahydroquinoline inhibited the dodecane decomposition the most. For example, after 40 min, 44 molar% of dodecane degraded in the absence of additives whereas only 10 molar% of dodecane degraded in the presence of tetrahydroquinoline.

2.Reaction kinetics The assumption of first-order kinetics was made for the reaction at 450°C from 10 to 40 min.[2] The first-order rate expression is given as:

$$dx/dt = k(1-x) \quad [1]$$

where x is the dodecane conversion, t is the time in seconds, and k is the first order rate constant in sec^{-1} . For isothermal reactions upon the integration, the following equation can be obtained:

$$\ln[1/(1-x)] = kt + c \quad [2]$$

If $\ln[1/(1-x)]$ is plotted against the time t, a straight line with a slope of reaction rate k can be obtained. Figure 34 represents the effects of additives on the rate constants of dodecane disappearance. The rate constant k of dodecane disappearance decreases in the order of dodecane neat > dodecane+5% tetralin > dodecane+5% benzyl alcohol > dodecane+5% 9,10-dihydrophenanthrene > dodecane+5% tetrahydroquinoline. In order to understand the hydrogen donor mechanism of these additives and have an accurate comparison between the additives, studies of additives based on moles instead of volume are in progress. In addition, new hydrogen donor additives are being screened to determine if a superior additive can be synthesized.

References

1. M.M. Coleman, L. Selvaraj, M. Sobkowiak, E. Yoon, *Energy & Fuels*, 1992, 6, 535-539.
2. P. Zhou, B.L. Crynes, *Ind.Eng.Chem.Process Des.Dev.*, 1986, 25, 508-514.

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

1. Characterization of Isolated Resinite Maceral (Contributed by David J. Clifford, Lei Hou, Jacqueline Bortiatynski, and Patrick G. Hatcher).

Introduction

The resinite maceral, which composes at least 5% of the Blind Canyon DECS-16 (Utah) coal, has previously been shown by spectroscopic techniques to be sesquiterpenoid in nature. The structure of sesquiterpenoid resinites has been shown to be comprised of a polycadinene-like polymer, which can be seen in Figure 35, as well as a significant portion of mobile bicyclic alkanes that are representative of the polycadinene backbone [1-3]. Because of the cycloparaffinic nature of sesquiterpenoid resinites and the thermal stability of these compounds, coals rich in resinite have been proposed to be possible precursors in the production of thermally stable jet fuel from coal. It is the purpose of this study to isolate the resinite maceral from the Blind Canyon coal by hand-picking and to analyze the pure product by both liquid and solid-state nuclear magnetic resonance spectrometry (NMR) as well as by pyrolysis/gas chromatography/mass spectrometry (py-GC/MS) to determine whether or not this resinite is actually composed of primarily a polycadinene polymer and a bicyclic sesquiterpenoid volatile fraction as suggested by other researchers. From this data it should then be possible to obtain a molecular model of the resinite maceral, which has been developed from the analytical data described below.

Experimental

The resinite maceral was isolated from the coal by hand-picking and purified by extraction with hexane. The hexane-soluble fraction, which contains the pure resinite, was filtered by passing it through a 0.2um filter attached to a 10mL syringe so that any

suspended particles or non-resinite material could be eliminated. The hexane was then evaporated from the resinite and the pure sample was dried in a drying oven at 110°C for 10 hours to remove any remaining solvent or moisture. Pyrolysis GC/MS was then carried out on the sample at temperatures of 710°C and 310°C for 10 s. The pyrolyzate was separated using a DB-17 capillary column that is directly coupled to a Dupont 21-490B mass spectrometer fitted with a Technivent Vector 1 data system for detection and compound identification. Sample masses of 0.414mg and 0.427mg were used in the pyrolysis of the Blind Canyon DECS-16 resinite at 710°C and 310°C, respectively.

Solid state ^{13}C NMR experiments employing cross polarization with magic angle spinning (CPMAS) and dipolar dephasing (DDMAS) were performed with the following experimental conditions. The samples were placed in the spinner of a Chemagnetics M-100 NMR spectrometer operating at a field strength of 2.35 T and spun at approximately 3.5 kHz. Data were collected in 0.5 K and zero-filled to 4 K with a pulse delay of 1 s for the CPMAS experiment over a sweep width of 10 Hz. 50 Hz of proton decoupling was applied as well as an exponential weighing factor of 10 Hz prior to Fourier transforming. A 1 ms contact time was used to ensure quantitative data and a dipolar dephasing delay of 60 μs was used to distinguish between methyl and methylene carbons as well as between protonated and non-protonated aromatic or olefinic carbons. Peak areas were measured using the Galactica Lab Calc curve fitting software package

Liquid NMR experiments were performed on a Bruker AM-300 spectrometer. Liquid samples were prepared by dissolving approximately 200mg of resinite in 2mL of deuterated chloroform or pyridine. The spectra obtained included a ^1H and broad band decoupled ^{13}C spectrum as well as a set of ^{13}C DEPT (distortionless enhancement by polarization transfer) spectra.

Results and Discussion

1. Pyrolysis-GC/MS. The pyrolysis spectra of the DECS-16 resinite at temperatures of 310°C and 710°C can be seen in Figure 36. Peak identifications can be found in Table 4. Pyrolyzing the resinite at 310°C, a temperature that is commonly used for the removal of mobile components of polymeric compounds, produces two distinct classes of pyrolyzates. The first class, which eludes between the retention times of 20 and 40 minutes, is composed primarily of bicyclic naphthalenes and hydronaphthalenes of varying degrees of saturation. The second group has been identified as cadinene dimers and occluded triterpenoids and eludes between the retention times of 50 and 75 minutes.

The analytical pyrolysis of the Blind Canyon resinite at 710°C yielded a larger distribution of pyrolyzates that are representative of a polycadinene-like compound.

These pyrolyzates, described above as the first class of compounds eluded, are primarily pentamethyl-bicyclic alkanes of varying degrees of saturation. Because these pyrolyzates are common to both spectra, it is unclear whether the dehydrogenation of the cycloparaffinic based polymer is an artifact of pyrolysis or whether these compounds are truly representative of the resinite structure, i.e. dehydrogenation is induced by the thermal maturation of the resinite. The cadinene dimers and triterpenoids in the 310°C pyrolysis spectrum are in nearly equal proportions to those observed in the 710°C pyrolysis spectrum, which suggests that the resinite is either composed of a large portion of volatile components or that the polymer itself is very unstable and thus is susceptible to fractionation by pyrolysis at very low temperatures, i.e. 310°C. It must be assumed, however, that all of the pyrolyzates of the 310°C spectrum are representative of the resinite structure and not induced by pyrolysis because of the low severity of pyrolyzing at 310°C.

2. Liquid and solid-state NMR. The conventional ^{13}C CPMAS NMR spectra of the whole coal and the results of the dipolar dephasing (DDMAS) can be seen in Figure 37. Evident in the CPMAS spectrum of the whole coal is the large contribution of the methyl carbons (resonating between 0 and 25ppm) to the total make-up of the coal. From this spectrum, the aromaticity of the Blind Canyon coal (DECS-16) has been calculated to be 0.65. In addition, the dipolar dephasing spectrum, shown in the bottom trace of Figure 37, has been used to identify the resonances between 25 and 50ppm as long chain methylene carbons and those between 100 and 130ppm as protonated aromatic or olefinic carbons.

Shown in Figure 38 are the ^{13}C CPMAS and DDMAS NMR spectra of an isolated resinite maceral. The aromaticity of the resinite was calculated to be 0.20, which means that the resinite structure is primarily aliphatic (80%). A DDMAS experiment with a dephasing delay of 60 μs resulted in resonances between 25 and 50 ppm, which are assigned to methylene carbons in addition to resonances between 110 and 120 ppm, which are assigned to olefinic carbons. Dipolar dephasing experiments with delays ranging from 2.5 μs to 200 μs were also obtained for this sample so that the ratio of protonated olefinic carbons to total olefinic carbons could be calculated. Figure 39 contains the areas of the peaks resonating between 110 and 150ppm in the DDMAS spectra of the Blind Canyon resinite. From this data, the ratio of protonated alkenes to total alkenes was found to be 0.24. A ratio of 0.24 corresponds to 1 out of every 4 olefinic carbons being protonated. The polycadinene structure contains 1 protonated olefinic carbon for every 2 olefinic carbons. The calculated ratio of 0.24 is most likely altered by the presence of non-polymeric occluded compounds having more than one

alkene within the whole resinite structure. To gain a better understanding of the resinite structure, the purified maceral was analyzed by liquid NMR.

The ^1H spectrum of the Blind Canyon resinite can be seen in Figure 40. Three distinct chemical shift regions are evident in this spectrum. The region between 0 and 3 ppm contains protonated aliphatic carbons, between 5 and 5.6 are protonated olefinic carbons, and the region between 6.7 and 7.2 ppm contains protonated aromatic carbons. Figure 41 is the broad band decoupled ^{13}C NMR spectrum of the resinite dissolved in deuterated pyridine (pyridine- D_6). Evident in this spectrum are the resonances from aliphatic carbons (0-60 ppm) and olefinic or aromatic carbons (100-160 ppm). In order to distinguish between methyl, methylene and methine carbons in the aliphatic region of the ^1H and ^{13}C spectra, a series of DEPT experiments was carried out; the corresponding pulse sequence is shown in Figure 42. The DEPT experiment, like a DDMAS experiment, is used to differentiate between the various types of protonated carbon species (i.e. methyl, methylene and methine). By choosing specified flip angles (45° , 90° and 135°), the resulting DEPT spectra will contain carbon signals that can be assigned to different carbon types. For example, a flip angle of 45° will produce signals from all carbon types while a flip angle of 90° will produce signals from only methine carbons. A 135° flip angle will produce negative peaks for methylene carbons and positive peaks for methyl and methine carbons. The DEPT spectra corresponding to flip angles of 45° , 90° and 135° can be seen in Figures 43, 44 and 45, respectively. From Figure 43, the spectrum that contains the majority of the resinite carbon, five different types of methine carbon can be assigned. These carbons have chemical shifts of 20, 26, 39, 47 and 127 ppm. Methylene carbons, of which there are two, resonate at 35 ppm and 130 ppm. The methyl carbons resonate at approximately 15 ppm and contribute significantly to the total make-up of this resinite.

Conclusions and Future Work

From the data presented above, it can be concluded that the DECS-16 resinite does indeed contain a substantial amount of occluded material, which appears to be cadinene dimers and triterpenoids, that is easily removed from the polymer backbone. Pyrolysis at 710°C increases the yield of bicyclic naphthalenes and hydronaphthalenes, suggesting that the polymeric make-up of this particular resinite is loosely based on polycadinene. It appears as if dehydrogenation induced by thermal maturation has occurred to some extent throughout the cadinene polymer. Solid-state NMR has shown that approximately 3 out every 15 carbons are olefinic and less than 1 of the three olefinic carbons is protonated, which again suggests a deviation from the polycadinene structure.

The data obtained from the liquid NMR analyses have aided in the assignment of carbon functional groups that can be qualitatively related to a cadinene polymer and will be essential in the quantitative work that follows.

In order to properly model the Blind Canyon DECS-16 resinite, it will be necessary in the future to remove the occluded material from the resinite polymer and repeat the experiments described above. The volatile compounds can then be analyzed by GC/MS, which will provide a better understanding of their contribution to the pyrolysis spectra as well as to the solid and liquid-state NMR spectra. With this data, it will then be possible to create a computer model of the resinite polymer that is consistent with all of the acquired analytical data and eventually to establish a computer model of the whole resinite.

References

- 1) Anderson K. B., Winans R. E. and Botto R. E. (1992) The nature and fate of natural resins in the geosphere-II. Identification, classification and nomenclature of resinites. *Org. Geochem.* **18**(6), 829-841.
- 2) Crelling J. C., Pugmire R. J., Meuzelaar H. L. C., McClennen W. H., Huai H. and Daras J. (1991) The chemical structure and petrology of resinite from the Hiawatha "B" coal seam. *Energy & Fuels* **5**, 688-694.
- 3) Meuzelaar H. L. C., Huai H., Lo R. and Dworzanski J. P. (1991) Chemical composition and origin of fossil resins from Utah Wasatch Plateau coal. *Fuels Proc. Techn.* **28**, 119-134.

2. Statistical Models for Bituminous Coal: A Three-Dimensional Evaluation of Structural and Physical Properties based on Computer-generated Structures (Contributed by Jean-Loup Faulon and P.G. Hatcher)

Introduction

Coal is a highly heterogeneous material. Its structure depends on the diverse composite material entering into its composition (minerals and macerals) and also on its degree of maturation (rank). Even within a single maceral and rank there is a considerable degree of complexity. Nevertheless, many attempts to model coal structure can be found in the literature. More specifically for high volatile bituminous coal, our subject of interest, the most commonly quoted models are the models of Given[1], Wiser[2], Solomon[3], and Shinn[4]. These models were constructed by a trial-and-error technique consisting of a

manual fitting of the analytical data. It is obvious that for each model the amount of data is small compared to the actual complexity of coal, and for all of the models more than one structure can be built. Hence, the process by which one structure is chosen instead of another is not clear. Actually all the authors agree that their structure was just intended to represent an "average" coal model. Average has a specific meaning in statistics, the mean value for a certain characteristic. This value can be calculated only if the size of the total population is known. Unfortunately, the size of the population of models was not estimated for the previously published structures, so "arbitrary" seems more appropriate than "average" as the word to characterize these structures.

Computer-aided molecular design (CAMD) has recently been introduced in the area of coal science[5-11]. Carlson and co-workers[5,6] used CAMD to model in three dimensions the previously published coal structures[1-4]. The structures were submitted to molecular mechanics and dynamics and potential energy, true density, and microporosity were evaluated for each model[7]. Nomura and co-workers have also used CAMD to study their own coal model[8]. Using molecular dynamics with periodic boundary conditions, Murata[9] correlated potential energy and true density. An important point needs to be mentioned regarding the utilization of CAMD for the study of coal. Prior to use of CAMD software, the connectivity (i.e. the structural formula) of the studied molecule has to be known. This information is unfortunately lacking for coal.

Many studies have been conducted in the past 25 years to resolve by computer the general problem of retrieving a structure from analytical data. The generic name for these studies is computer-aided structure elucidation (CASE)[12]. Efficient CASE systems are currently being investigated[13-16]. We recently developed a new CASE technique (the SIGNATURE program)[17] for the modeling of complex macromolecules. The technique is able to construct large molecular models from analytical structural data and has already been applied to devise models for kerogens[18], humic acids[19], and vitrinite from hvC bituminous coal[10,11]. In theory, any kind of quantitative and qualitative structural information can be introduced in the computer program. In practice, the computer technique successfully employs physicochemical analyses such as elemental analysis, functional group analysis, ^1H and ^{13}C NMR, and flash pyrolysis coupled with gas chromatography and mass spectrometry (flash pyrolysis/gc/ms). The first program to employ this technique was Xmol[20], whose purpose was to build randomly one 3D model from a set of analytical results. Generally, more than one model can be built from a set of analytical data, especially in the case of macromolecules such as coal. Knowledge of the number of possibilities is crucial for a true elucidation. A second program, the SIGNATURE program, was developed to accomplish true elucidation. The program is

based on an isomer generator[21] and is able to determine the number of possible models which can be built from a set of analytical data. Knowing the number of possibilities, the user can request depiction of one, several, or all the models. In a study of vitrinite from hvC bituminous coal, this program was used to generate 3D models for a molecule containing between 140 and 180 carbon atoms[11]. The analytical data used as input to the program were provided by elemental analysis, ^{13}C NMR and flash pyrolysis/gc/ms provided from a study by Hatcher et al.[22]. Even with this reasonably small number of atoms the number of possible models was enormous—about one million! It is clear that for coal, even for a specific rank and a pure maceral, the number of models is too large to build all of them, and too large to choose one model as representative of all the possibilities. Therefore, in such cases the following question needs to be considered: *how many structures and which structures must be selected and constructed?* The purpose of the present section is to answer this question.

Method

1. Generation of models from analytical data. As mentioned previously, two types of information are introduced in the computer program; quantitative and qualitative data. The quantitative data are provided by an accounting of all carbon, hydrogen, and oxygen atoms in terms of their functionality (e.g. aromatic, aliphatic, phenolic, carboxylic etc.). Typically this information is given by elemental analysis and ^{13}C NMR. The set of numbers counting the different atom types forms what we call the signature of the unknown macromolecule. The qualitative or molecular-level data are given by results of flash pyrolysis/gc/ms. From this analysis we can construct an assessment of molecular fragments and inter-fragment bonds which may exist in coal. The molecular fragments are the compounds determined by mass spectrometry; the inter-fragment bonds are the possible connections between the compounds as deduced from knowledge of pyrolysis mechanisms. If we ignore the bonds between two oxygen atoms, the typical inter-fragments bonds for coal are: *phenyl-phenyl*, *phenyl-alkyl*, *phenyl-oxygen*, *alkyl-alkyl*, and *alkyl-oxygen* [10,11].

The first task performed by the SIGNATURE program is to compute the quantity of each fragment and each inter-fragment bond to best match the quantitative data (the signature). This task is accomplished by solving the signature equation[17,18] The signature equation computes the pieces (fragments) and the relation between the pieces (inter-fragment bonds) of all possible models which are at that point still unresolved “puzzles”. To construct the models, the isomer generator provided by the SIGNATURE program is applied. Aside from constructing random models in three-dimensional space,

the isomer generator is also able to compute the number of models possible. Knowledge of this number is crucial to our being able to decide which model best represents coal. Even if this number is too large to allow the models to be built, sampling theory makes it possible to select a subset of models (a sample) which is statistically a good representation of the whole population[23]. Among the various techniques of sample design, the simple random sampling without replacement (SRSWOR) is the most convenient to apply here. The SIGNATURE program can directly build the required sample because the program allows us to construct non-identical random models.

2. Sample design. With the SRSWOR technique it is possible to define an optimal size for a sample[24] and extrapolate the mean sample value of a certain characteristic to the whole population (e.g. all the possible coal models). According to this theory of sampling, a sample of average structures can be defined, representing the studied coal. It is also possible to evaluate physical characteristics of this sample, such as the potential energy, the helium density, and the porosity, and to extrapolate these characteristics to the whole population of coal models.

Consider a population of size N from which a simple random sample of size n is drawn, without replacement. As applied in our study, N is the number of possible coal models, and n is the number of structures randomly built by the SIGNATURE program. Let $\bar{x}$ be the sample mean and let $\bar{X}$ and S^2 be the population mean and variance for a certain characteristic (the potential energy for example). It is known that $\bar{x}$ is an unbiased estimator and the following are true:

$$\bar{X} = \bar{x} \quad (I)$$

$$\text{Var}(\bar{x}) \leq (N-n) S^2 / Nn \quad (II)$$

By imposing the restraint

$$\text{Var}(\bar{x}) \leq V^* \quad (III)$$

for a prechosen constant V^* , n is determined to satisfy the inequality II. The n required is

$$n \geq NS^2 / (S^2 + NV^*) \quad (IV)$$

Prior information on S^2 is needed to determine the sample size using equation IV. Unfortunately such information is lacking in our study; it is not possible to know the variance of the potential energy for all the coal models. In such an instance the following stepwise procedure of Cochran[24] is used to determine the optimal value for the size of the sample:

1. Take an initial sample size n_1 (≥ 2). Calculate s_1^2 ; the variance of this sample. s_1^2 is an unbiased estimator of S^2 .

2. Calculate

$$n_2 = (s_1^2 / V^*) (1 + 2/n_1) \quad (V)$$

$$n = \max \{ n_1, n_2 / (n_2/N + 1) + 1 \} \quad (\text{VI})$$

3. Take $n - n_1$ additional observations if necessary. We can notice from the equations V and VI that $n = n_1$ if

$$V^* \geq s_1^2 (1 + 1/N - n_1/N) (1 + 2/n_1) / (n_1 - 1) \quad (\text{VII})$$

The procedure of Cochran[24] correlates the variance of the mean value for a certain characteristic and the sample size. Hence, for an arbitrary sample size, it is possible to determine the mean value for the population (equation I) the variance of this mean value (equation VII), and the population variance using the following equation (obtained from equation IV) :

$$S^2 \leq V^* Nn / (N - n) \quad (\text{VIII})$$

The procedure of Cochran has been applied for coal models to evaluate the means and variances for structural characteristics, energetics, and physical characteristics. For all these characteristics, means and variances were first evaluated for the sample and then extrapolated to the whole population using equations I, VII and VIII.

3. Structural characteristics. Molecular formula, molecular weight, molecular weight between cross-links, and number of aromatic fragments between cross-links are the structural characteristics of our coal models. Molecular formulas and molecular weights are directly computed by the SIGNATURE program for all structures built. The two last parameters are calculated for each structure from the number of cross-links in the structure, evaluated using the convention of Flory and Rehner[25]. Briefly, an aromatic fragment attached by two or less other fragments is not cross-linked, but 1/2 cross-link is created for each additional fragment attached. For example, an aromatic fragment attached to four other fragments will contribute to one cross-link.

4. Energetic characteristics. The potential energy and the non-bonded energy (sum of van der Waals, electrostatic, and hydrogen bond energies) are the energetic characteristics of our molecular models. These parameters are determined for the conformations that correspond to the minimum of energy for each model. The 3D structures generated by the SIGNATURE program are not initially at a minimum state of energy. To find a minimum energy conformation, the structures need to be submitted to molecular mechanics and dynamics simulations, using the computational methods provided by BIOGRAF software (Molecular Simulation Inc.). Molecular mechanics can be used to find the closest minimum for the potential energy starting from an initial conformation. In the present study, the potential energy was calculated using the Dreiding force field[26] and minimized using the classical conjugate gradient and steepest descents algorithms.

In reality molecules find their global minimum energy conformation by fluctuating about several configurations within energetic reach, as determined by the system temperature. These fluctuations are computer-simulated by what is called molecular dynamics. In the current study, the time step chosen for all molecular dynamics calculations was 1 fs and the dynamics simulations were performed for 60 ps at a constant 300 K temperature. It was observed that 60 ps was enough to locate a global minimum of energy. For all the structures the energy decreased only during the first 30 ps of the dynamics simulation and then remained approximately constant.

5. Physical characteristics. The helium density, the closed porosity volume, and the micropore volume are the physical characteristics measured for our coal molecular models. All these characteristics are calculated for energy minimized conformations obtained as described above.

The true density of a porous structure is the mass of a unit volume of the pore-free structure. Experimentally, the true density of coal is approximated using helium pycnometry. It is thus more appropriate to employ the term helium density. Using a technique already described in a previous report[7], we computer-simulated the calculation of the helium density by immersing the structure in a grid (of volume V_G) composed of cubic cells of 0.1 nm length. Briefly, the helium density is determined by dividing the molecular weight of the structure (MW) by the volume of the structure (V_s^{He}) and multiplying the result by Avogadro's number. The volume V_s^{He} is the volume not accessible to helium atoms and is the volumetric sum of three regions defined as atomic cells, internal cells, and closed cells (Figure 46). An atomic cell is a cell included in the van der Waals sphere of any atom. The sum of the volume of all atomic cells defines the atomic volume. Internal cells are cells not accessible to helium atoms because they are located between two or more atoms having an inter-atomic distance less than a critical value. The critical distance has been defined by Walker and co-workers[27] as the sum of the kinetic diameter of the diffusing species plus 0.16 nm. Recently, Rao[28] has calculated this critical size from the diffusion of different gases through carbon micropores. The values were determined using a Lennard-Jones (6-12) function to represent the atom-atom interactions. The critical value calculated for helium is 0.508 nm. Considering this result, we define an internal cell as a cell located between two atoms having an inter-atomic distance less than 0.508 nm. The sum of all internal cells defines the internal volume. Closed cells are determined after determining atomic and internal cells, and represent closed volumes (i.e. cells surrounded by atomic and internal cells). The sum of all closed cells defines the closed porosity volume. Since closed cells are not accessible to helium,

they must be included in the volume V_s^{He} if we are calculating the helium density and comparing it to experimentally determined values.

Microporosity is defined according to the method of Gan et al.[29]. The micropore volume (V_3) is the volume of pores having a diameter less than 1.2 nm, and is defined by the following equation:

$$V_3 = V_T - (V_1 + V_2) \quad (\text{IX})$$

where V_T is the total pore volume accessible to helium, V_1 is the volume of pores having a diameter greater than 30 nm, and V_2 is the volume of pores ranging between 1.2-30.0 nm in diameter. In our computer model, V_T is equal to the difference between the volume of the grid (V_G) and V_s^{He} . Thus,

$$V_T = V_G - V_s^{\text{He}} \quad (\text{X})$$

Our models are generally smaller than 30.0 nm, therefore, the volume V_1 is set to zero. The volume V_2 is determined using the grid method and a critical distance equal to 0.572 nm. This value, determined by Rao[28], is the critical distance for diffusion of nitrogen molecules through carbon micropores. Hence, V_2 is equal to the difference between the total volume of the grid and the volume of the structure not accessible to nitrogen molecule ($V_s^{\text{N}_2}$):

$$V_2 = V_G - V_s^{\text{N}_2} \quad (\text{XI})$$

By substituting equations X and XI into IX we obtain the following relationship defining the computer simulated micropore volume:

$$V_3 = V_s^{\text{N}_2} - V_s^{\text{He}} \quad (\text{XII})$$

One can argue that equations X and XI incorporate the volume of the grid which has no physical significance. However, V_3 , which represents the micropore volume, is determined using equation XII, which does not include the volume of the grid; hence, the micropore volume (V_3) can be correlated with experimental values.

Results

Our intention is not to present results for an "average" coal model but rather to focus exclusively on a sample of models for vitrinite from hvC bituminous coal. The experimental material chosen for this study was a piece of coalified wood, specifically a fossil stem which was recovered from a lacustrine shale from the Midland Formation (Triassic) near Culpeper, Virginia. In a previous report[22], we assumed that this sample is representative of vitrinite coalified to a rank of hvC bituminous coal. The analytical data supplied to the SIGNATURE program (published earlier[22]) are summarized in Table 5. The SIGNATURE program was run and all the solutions containing 333 carbon atoms were searched. This number of carbons was chosen considering the computational time and

the fact that all the fragments listed in Table 5 must be present in the models. The best solution of the signature equation ($C_{333}H_{302}O_{16}$) is listed in column 2 of Table 5. The deviation between model and analytical data is listed in column 3 of the same Table. The signature equation can provide a large number of solutions with different deviations between model and data. The program was asked to determine all the solutions containing 333 carbon atoms and having an average deviation between model and quantitative analytical data of less than one percent. Five solutions were found (Table 6). The average deviations between models and quantitative analytical data are listed in the last row of Table 6. Each solution contains the same quantity of each fragment as listed in Table 5, but different quantities of inter-fragment bonds.

The fragments which form the models are mainly alkylbenzenes and alkylphenols. As we have discussed in a previous publication[11], these types of fragments, when randomly connected, generate a highly cross-linked structure (molecular weight between cross-link less than 150 amu) with a high potential energy (more than 10 kcal/atom-mole). However, we also showed in the same study[11] that a systematic construction of hydroaromatic sub-structures built from the aromatic fragments allows one to increase the molecular weight per cross-link to an average of 1000 amu and to reduce the potential energy to about 2 kcal/atom mole.

Considering all of these previous observations, the SIGNATURE program was set up to build models using a two-stage procedure. First, a fragment was randomly chosen and successively connected to other fragments. The program retained only the combinations that formed new five- or six-membered rings. This first stage was repeated for all the fragments until there were no more possibilities of forming new ring systems. Using this procedure, the program constructed six disconnected hydroaromatic sub-structures using all the fragments and 81 inter-fragment bonds. At this point only a few inter-fragments bonds remained. These were used in the second stage to link or cross-link the hydroaromatic sub-structures. An illustrative example of this first stage procedure is diagrammed in Figure 47.

In the second stage, the final models were constructed by connecting and eventually cross-linking the hydroaromatic sub-structures together using the remaining inter-fragment bonds. Depending on the different solutions of the signature equation (cf. Table 6), the six hydroaromatic sub-structures were connected using five to nine remaining inter-fragment bonds. Figure 48 gives an example of this procedure for the case of model $C_{333}H_{302}O_{16}$ in which nine inter-fragment bonds remained after performing the first-stage operation.

Computing the number of possible non-identical models that can be constructed is time consuming; the problem has an exponential algorithmic complexity[21]. Limited by

the computational power of our workstation (Silicon Graphics 4D/320GTXB), the number of possible models was evaluated only for the second stage of the construction procedure (after building hydroaromatic sub-structures). Table 7 gives the number of possible models for each of the solutions of the signature equation; 319,318 is the total number of possible models that could be built during the second stage.

As presented in Tables 6 and 7 the population of possible coal models is subdivided into five different C_{333} structures, which represent five different solutions of the signature equation. To build a sample which is a good representation of the entire population, the sample size of each C_{333} structure has to be proportional to the corresponding population of all of its possible isomers. Considering the population size of each C_{333} structures (Table 7) and the computational time required to build the structures and evaluate the different characteristics, we chose to build a sample of $n_1 = 15$ structures comprising the following: 2 structures of $C_{333}H_{302}O_{16}$, 10 structures of $C_{333}H_{304}O_{16}$, 1 structure of $C_{333}H_{306}O_{16}$, 1 structure of $C_{333}H_{308}O_{16}$, and 1 structure of $C_{333}H_{310}O_{16}$. Five of these individual C_{333} structures, one for each of the five solutions of the signature equation are displayed in a three-dimensional representation in Figure 49 and in a schematic representation in Figure 50. For each of the 15 models, minimum energy conformations were calculated and structural, energetic, and physical characteristics were evaluated. The results are presented in Tables 8 and 9. Means and variances for the structural, energetic, and physical characteristics were calculated using the equations I to VIII defined above. The statistical results are listed in Table 10, and outlined below for the potential energy.

If $\bar{x}$ and s^2 are the sample mean and variance, and $\bar{X}$ and S^2 are the population mean and variance for the potential energy, then from Table 8 we can calculate $\bar{x} = 2.03$ kcal/atom-mole, and $s = 0.11$ kcal/atom-mole. Equation I allows us to write $\bar{X} = 2.03$ kcal/atom-mole. The population size is equal to the number of possible models ($N = 319,318$). Using equation VII the variance of the mean energy is evaluated for $n_1 = 15$; the variance is lower than 0.03 kcal/atom-mole. Finally the population variance is calculated using equation VIII; $S \leq 0.12$ kcal/atom-mole. In short, with a sample of 15 structures the mean potential energy of the entire population of models is 2.03 ± 0.03 kcal/atom-mole with a population deviation of 0.12 kcal/atom-mole.

Discussion

All 15 of the constructed C_{333} models match well with the quantitative analytical data with an average deviation of less than one percent. The cross-link densities found (Tables 8 and 10) are a direct consequence of the analytical data. From a structural point of

view, a cross-link is a bond between the hydroaromatic sub-structures (i.e. an inter-fragment bond). The total number of inter-fragment bonds determined by the signature equation depends on the quantitative analytical data; therefore, greater or lesser amounts of inter-fragment bonds would produce more or less cross-links and larger deviations between models and data. The number of cross-links varies only between 2.5 and 5 for each C₃₃₃ structure, and the molecular weight per cross-link averages 1205 amu with a standard deviation of 254 amu (Table 10). This value agrees well with swelling experiments for acetylated and pyridine extracted bituminous coal, where the molecular weight per covalent cross-link ranges between 900 and 1500 amu³⁰. Furthermore, the average number of aromatic fragments between cross-links (7.9) is in the range of values obtained from swelling experiments (4-8 aromatic fragments between cross-links)[30-35].

We can notice from Figure 51 that the potential energy increases slightly with the number of cross-links (1.85 kcal/atom for the model having 2.5 cross-links and 2.14–2.16 kcal/atom for the two models having 5 cross-links). The reverse trend is observed for the contribution of the non-bonded energy (49–51 % for the models having 2.5 cross-links and 57 % for the two models having 5 cross-links). However, overall, the energy values are clustered, and as a direct consequence, the variances are small (Table 10). Another interesting point was observed when the structures were depicted on the computer monitor. Independent of the cross-link density, the global conformations appeared very similar. As it is suggested by Figure 49, it was impossible to visually identify the structures containing the lower cross-link density. This suggests that even when the structures are not highly covalently cross-linked, they are held together by van der Waals interactions. A related observation is that no major changes in helium density and porosity were observed for the models investigated containing different cross-link densities (Figure 51).

The computed helium density averages 1.26 g/cc for all 15 C₃₃₃ structures constructed and the population deviation is less than 2 percent of this value. This result is in good agreement with experimental results found for vitrinite at a rank of bituminous coal (1.25 - 1.30 g/cc)[36]. The closed microporosity is almost non-existent for most of the 15 models and is lower than 7% of the total micropore volume. The computed micropore volume averages 0.030 cc/g with a population deviation of 13 percent. The micropore volume is slightly lower than experimental values found for HvC bituminous rank (0.039–0.070 cc/g)[29]. The low microporosity may be due to the size of our models; they are rather small compared to the particle sizes used in porosimetry experiments.

In summary, the physical properties that we have calculated agree well with experimental data. Further, the energetics and physical characteristics found for the different models are relatively close to each other and the variances are small. These

observations suggest that each model is in itself a reasonable representation of vitrinite. Perhaps the most important conclusion, however, is that we have been able to develop a technique that uses the power on the computer to create a number of molecular models for coal using actual quantitative and qualitative experimental data, and to show that the models, from a statistical viewpoint, are a good representation of the coal structure. Previous attempts at definitions of coal molecular structure, including previous computer models, necessarily included investigator bias and could not be proven to be representative or average coal structures. In the present study, we can conclude that for the physical properties investigated, a sample of 15 structures is sufficient to represent statistically the whole population of vitrinite from HvC bituminous.

References and Notes

1. Given, P. H., *Fuel* **1960**, 39, 147.
2. Wiser, W. H. *NATO ASI Series C* **1983**, 124, 325.
3. Solomon, P.R. *New Approaches in Coal Chemistry*, ACS Symposium Series No. 169; American Chemical Society: Washington, DC, 1981; pp 61.
4. Shinn, J. H. *Fuel* **1981**, 63, 1187.
5. Carlson, G. A. *Prepr. Pap. - Am. Chem. Soc. Div. Fuel Chem.* **1989**, 34(3), 780.
6. Carlson, G. A.; Granoff B. In *Coal Science II*: Schobert H. H., Bartle, K. D. Eds., ACS Symp. Ser. 461, Washington, DC, 1991, pp. 159.
7. Carlson, G. A. *Energy Fuels* **1992**, 6, 771.
8. Nomura, M.; Matsubayashi, K.; Ida, T.; Murata, S. *Fuel Process. Technol.* **1992**, 31, 169.
9. Murata, S. 1992, personal communication.
10. Faulon, J. L.; Hatcher, P. G.; Wenzel, K. A. *Prepr. Pap.- Am. Chem. Soc. Div. Fuel Chem.* **1992**, 37(2), 900.
11. Faulon, J. L.; Hatcher, P. G.; Carlson, G. A.; Wenzel, K. D. *Fuel Process. Technol.* in press.
12. Smith, D. H. *Computer-Assisted Structure Elucidation*: ACS Symp. Ser. 54, Washington, DC, 1977.
13. Christie, B. D.; Munk, M. E. *J. Am. Chem. Soc.* **1991**, 113, 3750
14. Bohanec, S.; Zupan, J. *J. Chem. Inf. Comput. Sci.* **1991**, 31, 531.
15. Bangov, I. P. *J. Chem. Inf. Comput. Sci.* **1992**, 31, 167.
16. Contretas, M. L.; Valdivia, R.; Rozas, R. *J. Chem. Inf. Comput. Sci.* **1992**, 31, 483.

17. Faulon, J. L. *Prediction Elucidation and molecular modeling : Algorithm and Application in Organic Geochemistry*, PhD Thesis, Ecole des Mines, Paris, 1991.
18. Faulon, J. L.; Vandenbroucke, M.; Drappier, J. M.; Behar, F.; Roméro, M. *Advances in Org. Geochem.* **1990**, *16*, 981.
19. Hatcher, P. G.; Faulon, J. L.; Clifford, D. J.; Mathews, J. P. Proceedings of the 6th IHSS Int. Meeting; Elsevier: Amsterdam, in press.
20. Faulon, J. L.; Vandenbroucke, M.; Drappier, J.M.; Behar F., Roméro, M. *Revue de l'I.F.P.* **1990**, *45*, 161.
21. Faulon, J. L. *J. Chem. Inf. Comput. Sci.* **1992**, *32*, 338.
22. Hatcher, P. G.; Faulon, J. L.; Wenzel, K. A.; Cody, G. D. *Energy Fuels* **1992**, *6*, 813.
23. Hajek, J. Sampling from a Finite Population; Marcel Dekker: New York, NY, 1981.
24. Cochran, W. G. Sampling Techniques (3rd Ed.); John Willey & Sons: New York, NY, 1977.
25. Flory, P. J.; Rehner, J. *J. Chem. Phys.* **1943**, *11*, 512.
26. Mayo, S. L.; Olafson, B. D.; Goddard, W. A. *J. Phys. Chem.* **1990**, *94*, 8897.
27. Walker, P. L., Jr.; Austin, L. G.; Nandi, S. P. In Chemistry and Physics of Carbon: Walker, P. L., Jr., Ed., Marcel Dekker: New York, NY, 1966; Vol. 2, pp. 257-371.
28. Rao, M. B. *Carbon* **1991**, 813.
29. Gan, H.; Nandi, S. P.; Walker, P. L., Jr. *Fuel* **1972**, *51*, 272.
30. Larsen, J. W.; Green, T. K.; Kovac, J. *J. Org. Chem.* **1985**, *50*, 4729.
31. Green, T. K.; Kovac, J.; Larsen, J. W. *Fuel* **1984**, *63*, 935.
32. Brenner, D. *Fuel* **1985**, *64*, 167.
33. Lucht, L. M.; Peppas, N. A. *Fuel* **1987**, *66*, 803.
34. Lucht, L. M.; Larsen, J. M.; Peppas, N. A. *Energy & Fuels* **1987**, *1*, 56.
35. Hall, P. J., Marsh, H.; Thomas, K. M. *Fuel* **1988**, *67*, 863.
36. Crelling, J. C. *Proc 1987 Int. Conf. Coal Sci.* **1987**, 119.

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

Introduction

The desirable roles of a catalyst in coal liquefaction are the prompt hydrogenation of the coal-derived reactive fragments (radicals) in the initial stage, and hydroprocessing of unsaturated compounds in the later stage. It has been recognized recently that

dispersed catalysts are superior to supported catalysts for primary hydroliquefaction of coal. The advantage of dispersed catalysts is largely due to their intimate contact with the surface of coal particles, which facilitates the activation and transfer of hydrogen to the coal-derived fragments and reactive sites. The present work deals with organometallic precursors which can directly produce dispersed bimetallic sulfides upon thermal decomposition on coal surface. Related to this work are two important general observations from previous investigations: 1) there could be synergistic effects between two different transition metal compounds [1-3] and, 2) for a given metal, an organometallic precursor may be better than an inorganic one for coal liquefaction [4,5].

It seemed to us that highly active bimetallic catalysts may be prepared from the "thiocubane" [6] clusters containing two different transition metals and sulfur 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. We realize that the bimetallic catalysts involved in this work would be rather expensive for use in an industrial process. However, knowledge of the dependence of catalyst activity on the structure and fundamental chemistry of the bimetallic precursors is important for the development of novel catalysts and advanced catalytic processes. Another potential application of new bimetallic precursors is the preparation of Co-Mo catalysts [7] which are usually prepared from inorganic salts [8]. The bimetallic precursors that are active for coal liquefaction may also be used for preparing hydrotreating catalysts for more efficient upgrading of coal liquids as well as residual oils to high quality gasoline, jet fuels and diesel fuels. In this paper we will report on a potential MoCo bimetallic sulfide dispersed catalyst system derived from a thiocubane cluster for promoting direct coal liquefaction.

Experimental

We synthesized three Mo-Co bimetallic thiocubane clusters as catalyst precursors, including $\text{Mo}_2\text{Co}_2\text{S}_4(\text{S}_2\text{CNEt}_2)_2(\text{CH}_3\text{CN})_2(\text{CO})_2$, $\text{Mo}_2\text{Co}_2\text{S}_4\text{Cp}_2(\text{CO})_2$, and $\text{Mo}_2\text{Co}_2\text{S}_4(\text{Cp}')_2(\text{CO})_2$, in which Et, Cp and Cp' represent ethyl, cyclopentadiene, and pentamethylcyclopentadiene, respectively. For convenience, we will refer to these three clusters as MoCo-TC1, MoCo-TC2, and MoCo-TC3, respectively. More details may be found elsewhere [9,10].

A Montana subbituminous coal (DECS-9) was obtained from Penn State/DOE Coal Sample Bank. It has the following composition: 76.1% C, 5.1% H, 0.9% N, 0.3% organic S, and 17.5% O on a dmmf basis. The loading for the bimetallic thiocubanes (see

below) was 0.5 wt% Mo on dmmf coal. When $\text{Mo}(\text{CO})_6$ and $\text{Co}_2(\text{CO})_8$ were used, the loading was 0.5 wt% for Mo and 0.3 wt% for Co metal based on dmmf coal. Temperature-programmed liquefaction (TPL) and non-programmed liquefaction were carried out in 25 mL microautoclaves at a final temperature of 400 °C for 30 minutes under an initial (cold) H_2 pressure of 7 MPa (1000 psi). Each reaction used 3 g dried coal (< 60 mesh) and 3 g of 1-methylnaphthalene (1-MN) as the solvent. The experimental details have been described recently [10,11]. 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

Figure 52 shows the structures of the three MoCo bimetallic thiocubane cluster precursors. We first prepared and tested MoCo-TC1, which was first synthesized and used by Halbert et al. [12,13] in preparing a hydrotreating catalyst. However, little catalytic effect was observed with this precursor, and the results suggest that the dithiocarbamate and acetonitrile ligands in MoCo-TC1 poison the resulting catalyst under the conditions employed [9]. This consideration prompted us to prepare the thiocubane which contains no nitrogen in the ligands, leading to the synthesis of MoCo-TC3 using the method of Brunner and Watcher [14], and subsequently the synthesis of MoCo-TC2 using the same procedure but with the simpler and cheaper C_5H_5 ligand. The basic differences between these three thiocubanes are the type of ligands bound to the Mo. MoCo-TC2 impregnated from toluene afforded much higher conversion and oil yield; it is much more active than MoCo-TC1 [9]. The core structure and ligands of MoCo-TC3 and MoCo-TC2 are of the same nature, except that the pentamethylcyclopentadiene ligand in MoCo-TC3 is replaced by cyclopentadiene in MoCo-TC2. Under both conventional and temperature-programmed liquefaction (TPL) conditions, MoCo-TC2 is better than MoCo-TC3 in terms of higher coal conversion [10]. Overall, the above results demonstrate that MoCo-TC2 is the best bimetallic precursor among the thiocubanes. We now turn to the effect of the loading method for MoCo-TC2.

As Weller (15) pointed out in 1982, the degree of dispersion is very important for the performance of unsupported catalysts in coal liquefaction. In the present study we examined four different methods for dispersing MoCo-TC2 in TPL. The advantages of TPL have been demonstrated in our recent reports [10,11]. The TPL conditions used in this work consist of a rapid heat-up to 200 °C, soaking at 200 °C for 15 min, programmed heat-up from 200 to 400°C at about 5 °C/min, followed by a 30 min holding period. Since the thiocubane precursor MoCo-TC2 may not be very active by itself, its

decomposition at low temperature, which could serve as an in-situ activation/generation of the active catalyst, could contribute to more effective hydrogenation of reactive fragments and aromatics at high temperature.

Figure 53 shows that even the physical mixing of MoCo-TC2 with coal strongly enhanced coal conversion under TPL conditions. This, however, must be interpreted with caution, because MoCo-TC2 is soluble in 1-MN, which is the reaction solvent. In the second method, we first dissolved MoCo-TC2 in 1-MN, and then added coal to the solution; this mixture was directly subjected to reaction. Figure 53 indicates that the two methods gave essentially identical results. It is also clear from Figure 53 that both physical mixing and using a solution of MoCo-TC2 in 1-MN afford similar results to the MoCo-TC2 impregnated from toluene solution. A question that arises is can we further improve the catalytic activity?

We believe that low-rank coals are macromolecular in chemical nature but microporous in physical nature. Because of its relatively large molecular size (Figure 52), the diffusion of MoCo-TC2 molecules into the interior of coal particles through pores may be difficult in 1-MN and toluene. With an attempt to improve the catalyst dispersion on coal by using a swelling solvent, we dissolved MoCo-TC2 in a mixture of tetrahydrofuran (THF) and toluene (vol: 50:50), with about 4-5 mL of the binary solvent added per g of coal. This mixture was stirred under N_2 for about 20 h, followed by rotary evaporation of the solvent and vacuum drying at 100 °C for over 2 h. This impregnation method was the most effective, as reflected by considerably higher conversion and higher oil yield than the other three methods. These results indicate that proper dispersion is important for MoCo-TC2. It has been shown that using proper swelling solvents such as THF and tetrabutylammonium hydroxide for impregnation of metal carbonyls and ATTM on coal could enhance the coal conversion [16,17]. Good swelling solvents probably result in the expansion of the microporous structure and thus enables better dispersion of catalyst precursors, which leads to improved hydrogen transfer to coal-derived radicals [16].

In order to evaluate the activity level of the bimetallic precursor relative to the mixture of two corresponding metal compounds, we also examined the catalytic activities of $Mo(CO)_6$, $Co_2(CO)_8$, their mixture, and their mixture plus added sulfur. Using either one alone increased coal conversion by a similar amount [9]. Combination of the two metal compounds gives significantly higher conversion than either $Mo(CO)_6$ or $Co_2(CO)_8$ alone.

Figure 54 shows the results of TPL of the coal impregnated with $Mo(CO)_6 + Co_2(CO)_8$ and MoCo-TC2. Both types of precursors were impregnated onto the coal from

their THF-toluene solution, as described above. Using mixed metal carbonyls increased coal conversion from 34 to 71 wt%. Adding elemental sulfur further enhanced the conversion and oil production to 83 to 41 wt%, respectively. However, the highest conversion, 92 wt%, and the highest oil yield, 47 wt%, were obtained with the single molecular precursor, MoCo-TC2. These results suggest that the composition and structure of precursors are important for achieving high catalytic activity of the resulting dispersed catalyst.

Summary

The results indicate that the structure of the precursors, in particular the type of ligands bound to the metal species, affect the activity of the resulting bimetallic MoCo sulfide catalyst significantly. For a given precursor, the solvents and methods used for catalyst impregnation also affect coal conversion. Among the M-M' type precursors tested, $\text{Mo}_2\text{Co}_2\text{S}_4(\text{Cp})_2(\text{CO})_2$ (MoCo-TC2) impregnated onto coal from toluene-THF, generated in-situ the best catalyst for coal liquefaction. The thiocubane cluster MoCo-TC2 is a promising precursor to the bimetallic sulfide catalyst.

References

1. Derbyshire, F.J.; *Energy & Fuels*, 1989, 3, 273-277, and references cited therein.
2. Garg, D.; Givens, E.N.; *Fuel Process. Technol.*, 1984, 8, 123-134.
3. Nomura, M.; Miyake, M.; Sakashita, H.; Kikkawa, S., *Fuel*, 1982, 61, 18-20.
4. Hirschon, A.S.; Wilson, R.B.; *Am. Chem. Soc. Sym. Ser.*, 1991, 461, 273-283.
5. Hirschon, A.S.; Wilson, R.B.; *Fuel*, 1992, 71, 1025-1031.
6. Mingos, D.M.P.; Wales, D.J., "Introduction to Cluster Chemistry", Prentice Hall: Englewood Cliffs, New Jersey, 1990, 318 pp.
7. Chianelli, R.R.; Daage, M.; Halbert, T.R.; Ho, T.C.; Stiefel, E.I., *Am. Chem. Soc. Div. Petrol. Chem. Prepr.* 1990, 35 (2), 227-231.
8. Song, C.; Nihonmatsu, T.; Nomura, M., *Ind. Eng. Chem. Res.*, 1991, 30, 1726-1734.
9. Song, C.; Parfitt, D.S.; Schobert, H. H.; *Catalysis Letters*, 1993, in press.
10. Song, C.; Parfitt, D.S.; Schobert, H. H.; *Am. Chem. Soc. Div. Fuel. Chem. Prepr.* 1993, 38(2), 546-553.
11. Song, C.; Schobert, H. H.; Hatcher, P. G., *Energy & Fuels*, 1992, 6, 326-328.
12. Halbert, T. R.; Cohen, S. A.; Stiefel, E. I., *Organometallics* 1985, 4, 1689-1690.
13. Halbert, T.R.; Ho, T. C. Stiefel, E. I.; Chianelli, R. R., Daage, M., *J. Catal.* 1991, 130, 116-119.
14. Brunner, H.; Wachter, J., *J. Organomet. Chem.* 1982, 240, C41-44.

15. Weller, S.W. Coal Liquefaction with Molybdenum Catalysts. Review Paper presented at the 4th Int. Conf. Chem. Uses of Mo., Golden, Colorado, Aug. 9-12, 1982.
16. Joseph, J.T., Fuel, 1991, 70, 139-144; 459-464.
17. Artok, L.; Davis, A.; Mitchell, G.D.; Schobert, H.H., Energy & Fuels, 1993, 7, 67-77.

APPENDIX 1
TABLES

Table 1. Yield of Liquids and Solids and Pressure Build Up from Thermal Stressing Experiments of JPTS Jet Fuel.

Sample liquid-10 ml solid-100 mg	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, %
JPTS in N ₂	63	4.2	600	-
JPTS + PX-21 in N ₂	0	5.5	300	51
JPTS in air	70	3.5	500	-
JPTS + PX-21 in air	0	5.0	300	105

Table 2. Comparison of Measured Activation Energies for Filament Growth with Those for Carbon Diffusion in the Corresponding Metal Catalysts. [48 and the References Therein]

Catalyst	Activation Energy For	
	Catalyzed Filament Growth kcal / mole	Diffusion of Carbon kcal / mole
Nickel	34.7	33.0 - 34.8
a-Iron	16.1	10.5 - 16.5
Nickel - Iron	33.6	34.0
Cobalt	33.0 - 33.3	34.7
Vanadium	27.6	27.7
Molybdenum	38.8	41.0
Chromium	27.1	26.5

Table 3. Typical Properties of Some Carbonaceous Deposit. [39]

Type of Carbon	Typical Temperature of Formation (°C)	d Spacing (Å)	L _c (Å)	L _a (Å)	C/H Atomic Ratio
Gas phase	1000	3.61-3.70	12.2	42	8
Surface	1000	3.46-3.54	28	51	> 80
Catalytic (Laminar)	600	3.37	200	400	20
Graphite		3.35	∞	∞	∞

Table 4. Assignments of Peaks Labeled in 310 and 710°C Pyrolysis Spectra.

Peak Number	Retention Time (min)	Peak assignment
1	22.63	C5-octahydronaphthalene (T)
2	23.00	C4-tetrahydronaphthalene (T)
3	23.72	C5-octahydronaphthalene (T)
4	23.93	C5-octahydronaphthalene (T)
5	24.10	C5-octahydronaphthalene (T)
6	25.03	C5-hexahydronaphthalene (T)
7	25.24	C5-octahydronaphthalene (T)
8	25.45	C5-naphthalene (T)
9	26.46	C5-hexahydronaphthalene (T)
10	26.63	C5-naphthalene (T)
11	27.01	1,2,3,4-tetrahydro-2,2,5,7-tetramethylnaphthalene (N)
12	28.14	C5-tetrahydronaphthalene (T)
13	28.19	C5-dihydronaphthalene (T)
14	29.44	C5-tetrahydronaphthalene (T)
15	34.37	1,4-dimethyl-7-(1-methylethyl)-azulene (N)

T = tentative identification; N = NBS Wiley Library identification.

Table 5. Quantitative and Qualitative Analytical Data for HvC Bituminous Coalified Wood (Midland Stem). [22]

Parameter	Analytical Data	Model (C ₃₃₃ H ₃₀₂ O ₁₆)	Deviation Analytical data - Model
<u>Quantitative data (normalized for 100 carbon atoms)</u>			
C	100.0	100.0	-
H	92.0	91.8	0.2
O	5.0	4.6	0.4
f _a	62.5	63.0	-0.5
f _a ^H	28.0	27.6	0.4
f _a ^P	7.5	7.5	0.0
f _{al}	37.5	37.4	0.1
f _{al} ^H	26.0	26.2	-0.2
f _{al} [*]	11.5	11.2	0.3
Average deviation			± 0.26
<u>Qualitative data (weight % normalized to total aromatic fragments)</u>			
benzene	3.3	2.0 (1)	1.3
toluene	4.8	4.8 (2)	0.0
C-2 benzenes	5.2	8.3 (3)	-3.1
C-3 benzenes	3.9	6.3 (2)	-2.4
phenol	3.6	2.5 (1)	1.1
<i>o</i> -cresol	5.7	2.8 (1)	2.9
<i>m</i> + <i>p</i> -cresol	13.0	8.5 (3)	4.5
2,4 dimethylphenol	12.0	9.6 (3)	2.4
other C-2 phenols	10.3	6.4 (2)	3.9
C-3 phenols	10.9	14.2 (4)	-3.3
C-4 phenols	4.8	3.9 (1)	0.9
alkylnaphthalenes	17.0	24.4 (6)	-7.4
alkyldibenzofurans	5.2	6.2 (1)	-1.0
methyl	-	(7)	
ethyl	-	(9)	
propyl	-	(3)	
C4-C22	-	(0)	

f_a = aromatic carbon, f_{al} = aliphatic carbon, f_a^H = protonated aromatic carbon, f_a^P = phenolic or phenolic ether, f_{al}^H = aliphatic carbon in CH or CH₂, and f_{al}^{*} = aliphatic carbon as methyl. As mentioned in the text, the weight percentages given by pyrolysis results are not an accurate representation of the quantities of fragments present in coal. For this reason, the values listed here are not taken quantitatively, and the SIGNATURE program considers the list of fragments only as qualitative information. Values indicated in parentheses are the quantities of each fragment corresponding to a molecule containing 333 carbon atoms.

Table 6. Solutions of the Signature Equation.

Inter-fragment bonds	C ₃₃₃ H ₃₀₂ O ₁₆	C ₃₃₃ H ₃₀₄ O ₁₆	C ₃₃₃ H ₃₀₆ O ₁₆	C ₃₃₃ H ₃₀₈ O ₁₆	C ₃₃₃ H ₃₁₀ O ₁₆
<i>phenyl-phenyl</i>	5	5	5	5	5
<i>phenyl-alkyl</i>	29	29	29	29	28
<i>phenyl-oxygen</i>	9	9	9	9	9
<i>alkyl-alkyl</i>	41	40	39	38	38
<i>alkyl-oxygen</i>	6	6	6	6	6
Total	90	89	88	87	86
Average deviation ^a	0.26	0.29	0.39	0.49	0.71

^a The deviation is the average deviation between model and quantitative analytical data as calculated in Table 1.

Table 7. Population Information for Each Solution of the Signature Equation.^a

Molecular Formula	Number of possible models
C ₃₃₃ H ₃₀₂ O ₁₆	52,272
C ₃₃₃ H ₃₀₄ O ₁₆	231,000
C ₃₃₃ H ₃₀₆ O ₁₆	24,750
C ₃₃₃ H ₃₀₈ O ₁₆	9,856
C ₃₃₃ H ₃₁₀ O ₁₆	1,440

^a The numbers of possible models have been estimated using the isomer generator²¹ provided by the SIGNATURE program for the second stage of the construction procedure as described in the text.

Table 8. Structural Characteristics for Each of the 15 Individual Models Comprising the Sample.

Model No.	Molecular Formula	Number of Covalent Cross-Links ^a	Molecular Weight between Cross-links	Number of Aromatic Fragments between Cross-links ^b
1, 2	C ₃₃₃ H ₃₀₂ O ₁₆	5	911	6
3-12	C ₃₃₃ H ₃₀₄ O ₁₆	4	1139	7.5
13	C ₃₃₃ H ₃₀₆ O ₁₆	3	1519	10
14	C ₃₃₃ H ₃₀₈ O ₁₆	3	1520	10
15	C ₃₃₃ H ₃₁₀ O ₁₆	2.5	1825	12

^a The number of cross-links has been calculated using the convention of Flory and Rehner²⁵.

^b The total number of aromatic fragments is 30, the sum of the computed quantities of aromatic fragments listed in Table 1 (column 2 values indicated in parentheses).

Table 9. Energetics and Physical Characteristics for Each of the 15 Individual Models Comprising the Sample.

Model No	Minimized Energy kcal/ (atom mole)	Non-bonded Energy / Total Energy	Helium Density (g/cc)	Micropore Volume (cc/g)	Closed Porosity (cc/g)
1	2.14	0.51	1.26	0.032	< 0.001
2	2.16	0.49	1.27	0.031	< 0.001
3	2.07	0.52	1.26	0.031	0.001
4	2.06	0.52	1.25	0.032	< 0.001
5	2.01	0.51	1.28	0.035	< 0.001
6	1.99	0.53	1.26	0.026	0.001
7	2.09	0.53	1.27	0.033	< 0.001
8	1.93	0.55	1.25	0.029	< 0.001
9	2.23	0.47	1.23	0.028	0.001
10	2.11	0.54	1.29	0.035	< 0.001
11	2.07	0.51	1.25	0.033	0.002
12	1.94	0.56	1.27	0.034	< 0.001
13	1.93	0.53	1.25	0.029	0.001
14	1.89	0.54	1.23	0.032	0.002
15	1.85	0.57	1.26	0.022	0.001

Table 10. Statistical Results for Structural and Physical Characteristics for the Whole Population of Vitrinite Models from HvC Bituminous Coal.

Parameter	Population Mean ^a	Population Deviation ^b
Number of cross-links	3.9 ± 0.2	1.65
Molecular weight between cross-links (amu)	1205 ± 66	254
Number of aromatic fragments between cross-links	7.9 ± 0.3	1.3
Minimized energy (kcal/ atom mole)	2.03 ± 0.03	0.12
Non-bonded energy/ total energy	0.53 ± 0.01	0.03
Helium density (g/cc)	1.26 ± 0.01	0.02
Micropore volume (cc/g)	0.030 ± 0.001	0.004

^a Determined using equations I and VII

^b Determined using equation VIII.

Table 11. Catalytic Liquefaction of DECS-9 Subbituminous Coal.

Catalyst precursor	Solvent for catalyst loading ^a	In-situ pretreat at LT ^b	Reaction temp, °C	<u>Oil + Gas</u> dmmf wt%	<u>Asphalt</u> dmmf wt%	<u>Preasph.</u> dmmf wt%	<u>Conv.</u> dmmf wt%
None	None	No	400	16.0	9.4	6.8	32.2
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
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
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

FIGURES

Figure 1. Effects of Initial Sample Volume of n-C₁₄ (at Room Temperature) on Its Pyrolysis at 450 °C for 30 min under Different Pressure of UHP N₂ in 25 mL Microreactor.

Figure 2. Effects of Initial N₂ Pressure at Room Temperature on Pyrolysis of n-C₁₄ with Different Initial Sample Volume at 450 °C for 30 min in 25 mL Microreactor.

Figure 3. Measurements of solid particle and deposit formation in mixtures of JP8C and Tetradecane containing 18.45 wt% Tetradecane, at 450°C under nitrogen over periods from 2 to 24 hours: a. Mass of deposit formed at the top of the reactor tube. b. Mass of deposit formed on the bottom of the reactor tube. c. Mass of deposit formed on the vertical walls of the reactor tube. d. Mass of suspended particles removed from the liquid by filtration.

Figure 4. Liquid Products from Thermal Stressing of JPTS Jet Fuel with and without PX-21 Activated Carbon at 450°C in Air Atmosphere.

400 μm

Position a

200 μm

Position b

Figure 5. Polarized-Light Micrographs of PX-21 after Stressed with JPTS at 450°C in Air Atmosphere.

400 μm
Position a

400 μm
Position b

Figure 6. Polarized-Light Micrographs of Deposit Obtained after Thermal Stressing of JPTS at 450°C in Air Atmosphere.

Figure 6. (Continued) Polarized-Light Micrographs of Deposit Obtained after Thermal Stressing of JPTS at 450°C in Air Atmosphere.

JPTS+PX-2 JPTS, 425°C
425°C, in N₂ in N₂

JPTS+PX-21, JPTS, 425°C
425°C, in air in air

Figure 7. Liquid Products from Thermal Stressing of JPTS Jet Fuel with and without PX-21 Activated Carbon at 425°C in Nitrogen and Air Atmosphere.

Figure 8. Gas Chromatograms of Unstressed JPTS, JPTS Stressed Alone and JPTS Stressed with PX-21 at 425°C in Nitrogen.

Figure 9. Gas Chromatograms of Unstressed JPTS, JPTS Stressed Alone and JPTS Stressed with PX-21 at 425°C in Air.

Figure 10. Polarized-Light Micrographs of Deposit Obtained after Thermal Stressing of JPTS at 450°C in Nitrogen Atmosphere.

Figure 11. Polarized-Light Micrographs of Deposit Obtained after Thermal Stressing of JPTS at +25°C in Air Atmosphere.

Figure 12. Relationship between Rate of Deposit Formation with Temperature from Air-Saturated Jet Fuels at 69 ATM: • JP-5 (64 ppm of O_2); ○ Blend Fuel (77 ppm O_2). [8]

Figure 13. Constant Heat Flux Flow Reactor. [31]

Figure 14. Constant Surface Temperature Flow Reactor. [28]

Figure 15. Mechanism of Filamentous Carbon Formation:
(A) Classical Model;
(B) Extrusion Mode. [48]

Figure 16. Relationship between Rate of Catalytic Carbon Formation with Temperature for Butene/ Ni Foil, $P_{C_4H_8} = 100$ Torr, $P_{H_2} = 25$ Torr. [49]

Figure 17. Variations of the Mechanism of Filamentous Carbon Formation: (a) Bulk Metastable Carbide Model; (b) Surface Metastable Carbide Model. [53]

Figure 18. Mechanism of PAHs and Soot Formation via Acetylene Polymerization and Dehydrogenation. [95]

Figure 19. General Mechanisms for Soot Formation. [96].

Figure 20. Growth Modes of Pyrolytic Carbon: (a) On a Substrate Asperity; (b) On Regenerative Substrate Surfaces. [110]

Figure 21. Overview of Deposits Formation on Stainless Steel Surfaces as a Function of time. [117]

Figure 22. Schematic Diagram of the Mechanisms of Catalytic and Non-Catalytic Carbon Deposit Formation in Pyrolysis of Hydrocarbons, LT, Low Temperature: $< 400^{\circ}\text{C}$; MT, Intermediate Temperature: $400\text{--}800^{\circ}\text{C}$; HT, High Temperature: $> 800^{\circ}\text{C}$.

Figure 23. Comparative Plots for Molar Yield % of C6 to C10 n-paraffins Obtained on Stressing Dodecane Neat and Dodecane + 5% Benzyl Alcohol at 425°C under 100 psi Air 0, 1, 3, 6 h and 12h.

Figure 24. Comparative Plots for Molar Yield % of C6 to C10 n-paraffins Obtained on Stressing Dodecane Neat and Dodecane + 5% Benzyl Alcohol at 425°C under 100 psi Air 0, 1, 3, and 6 h.

Figure 25. Molar Yield of Product Hydrocarbon Gases on Stressing Dodecane Neat and Dodecane + 5% Benzyl Alcohol at 425°C under 100 psi Air.

Figure 26. (Top) Shows Mole % of Benzyl Alcohol Remaining in the Sample:
(Bottom) Mole % of Dodecane Remaining in the Samples Stressed at 452°C
under 100 psi Air for 1, 3, 6, and 12 h.

Figure 27. Molar Yield % of Benzyl Alcohol and its Products Obtained on Stressing Dodecane + 5% Benzyl Alcohol at 425°C under 100 psi air for 1, 3, and 6 h.

Figure 28. Primary Reaction Scheme for the Degradation of Dodecane in the Presence of Benzyl Alcohol.

Figure 29. Molar Yield % of Product C6 and C11 Alkanes Obtained on Stressing Deuterated Dodecane at 425°C under 100 psi Air for 3 h.

Figure 30. Molar Yield % of Product C6 and C11 Alkanes Obtained on Stressing Deuterated Dodecane + 5% Benzyl Alcohol at 425°C under 100 psi Air for 3 h.

Figure 31. Molar Yield % of Product Alkenes C6 to C11 Obtained on Stressing Deuterated Dodecane + 5% Benzyl Alcohol at 425°C under 100 psi Air for 3 h.

Figure 32. Molar Yield of Product Alkenes C6 to C11 Obtained on Stressing Deuterated Dodecane at 425°C under 100 psi Air for 3 h.

Figure 33. Effects of Hydrogen Donor Additives on the Molar % Conversion of Dodecane at 450-C Under Initial N₂ Pressure of 1.0 MPa (145 psi).

Figure 34. Effects of Hydrogen Donor Additives on the Rate of Dodecane Decomposition at 450°C Under Initial N₂ Pressure of 1.0 MPa.

Figure 35. Cadinene and Polycadinene Structures.

310C pyrolysis of DECS-16 resinite

710C pyrolysis of DECS-16 resinite

Figure 36. Pyrolysis-GC/MS Spectra of DECS-16 Resinite.

Figure 37. a) ^{13}C CPMAS Spectrum of the DECS-16 Whole Coal. b) ^{13}C DDMAS Spectrum of the DECS-16 Whole Coal.

Figure 38. a) ^{13}C CPMAS Spectrum of the Resinite Hand Picked from DECS-16 Coal.
b) ^{13}C DDMA Spectrum of the Hand Picked Resinite from the DECS-16 Coal.

Figure 39. Olefinic Area (110-150 ppm) vs Dipolar Dephasing Delay.

Figure 40. ^1H Solution NMR Spectrum of the Resinite Dissolved in CCl_3D .

Figure 41. ^{13}C Solution NMR Spectrum of the Resin Dissolved in Pyridine- D_6 .

Figure 42. DEPT Pulse Sequence.

Figure 43. ^{13}C Solution NMR Spectrum of Resinite Dissolved in CCl_3D Measured by 45° DEPT Pulse Sequence.

53.341
50.064
48.056
42.885
38.364
38.239
38.083
37.249
32.320
30.745
28.478
27.821
26.206
21.405
20.000
19.256

75.988

121.426
124.513
127.158
127.646
PPM

BRUKER
L03

AU PR 3
DEPT AUR
DATE 5-6-93

SF 75 469
SY 112.0
O1 5895 020
SI 32768
TO 32768
SM 12195 122
HZ/PT 744

PW 0 0
RD 0 0
AQ 1 34.3
RG 800
NS 16845
TE 297

FW 15700
O2 4900.000
DP 22M 00

LB 10 000
GB 0 0
CX 40 00
CY 0 0
F1 150 82.3P
F2 -10 601P
HZ/UM 334 562
PPM/UM 4 036
GR 0.11 0.7

Figure 44. ^{13}C Solution NMR Spectrum of Resinite Dissolved in CCl_3D Measured by 90° DEPT Pulse Sequence.

15.148
 17.407
 19.712
 21.479
 25.173
 28.133
 29.478
 31.039
 35.070
 38.023
 40.840
 48.945
 53.399

75.975

121.893
 125.329
 126.870

ppm

AU PROJ: L02
 DEPT: AUR
 DATE 5-6-93

SF 75.469
 SY 112.0
 O1 5895.020
 S1 32768
 T0 32768
 SM 12195.122
 HZ/PT 744

PM 0.0
 RD 0.0
 AQ 1.343
 RG 800
 NS 20278
 TE 297

FM 15300
 O2 4900.000
 UP 228.00

LB 10.000
 GB 0.0
 CX 40.00
 CY 0.0
 F1 150.004P
 F2 -9.980P

HZ/FM 301.845
 PPM/FM 4.000
 LB 6.13.90

Figure 45. ^{13}C Solution NMR Spectrum of Resinite Dissolved in CCl_3D Measured by $^{135}^\circ$ DEPT Pulse Sequence.

Figure 46. 2D projection of the grid system used to calculate helium density, and porosity. The disks are the projections of the van der Waals spheres for the atoms. The double arrow represents the critical distance which defines internal cells.

Figure 47. An example depicting the construction of a hydroaromatic sub-structure. The initial fragments (top of the figure) are fragments identified by pyrolysis/gc/ms analysis. The dashed lines represent the bonding sites. Our models are built using between 86 and 90 inter-fragment bonds as determined by the signature equation (Table 6). Each inter-fragment bond requires two bonding sites to be created, and therefore the number of bonding sites for all the fragments must range between 172 and 180. The bonding sites were chosen arbitrarily. Overall, there is a total of 49 fragments. This gives an average number of bonding sites per fragment ranging between 3.5 and 3.7. At the bottom right of the figure is a schematic representation of the final sub-structure. In this representation, the initial aromatic fragments are represented by cross-hatched circles, the double edges between two fragment indicates that the fragments are linked by new six and/or five membered rings, the dashed lines are the remaining bonding sites.

Figure 48. Example of connection of hydroaromatic sub-structures. The schematic representation used in this figure is described in the caption of Figure 47. Using the convention of Flory and Rehner[25], there are 5 cross-links in this structure. The location of each 1/2 cross-link is noted by an arrow.

Figure 49. Three-dimensional representations of five of the models constructed. The displayed models are: models No 1, 3, 13, 14, and 15. All these models have been submitted to molecular mechanics and dynamics simulations, and the figure represents the minimum energy conformations.

Figure 50. Schematic representation of the five of the models constructed.

Figure 51. Correlation between physical characteristics and cross-link densities for each of the 15 individual models comprising the sample. These graphs have been drawn from the results given in Tables 8, 9, and 10. For each graph, the horizontal line represents the population mean.

Figure 52. Structure of the Three Different Bimetallic Thiocubane 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 53. Effect of methods for dispersing MoCo-TC2 in the liquefaction of DECS-9 coal under TPL conditions (200 °C for 15 min, programmed heat-up at 5°C/min, 400°C for 30 min).

Figure 54. Comparison of catalytic activity of MoCo-TC2 with that of mixed metal carbonyls and the mixture plus added sulfur for liquefaction of the DECS-9 coal (TPL at final temperature of 400°C). All the catalysts were impregnated from THF-toluene solution.

END

**DATE
FILMED**

3 / 22 / 94