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STUDIES IN COAL LIQUEFACTION WITH APPLICATION TO THE SRC AND RELATED PROCESSES

Quarterly Report for the Period November 1981—January 1982

By
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Work Performed Under Contract No. AC22-79ET13397

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U. S. DEPARTMENT OF ENERGY

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PREPARED FOR THE UNITED STATES DEPARTMENT OF ENERGY
Under Contract No. DE-AC01-79ET13397

Objective and Scope

Scope:

The Auburn Coal Conversion Laboratory is engaged in a research program designed to investigate fundamental aspects of the Solvent Refined Coal (SRC) and other closely related coal liquefaction processes. The SRC process provides a method for liquefaction of coal, and removal of sulfur and ash pollutants which would results from direct combustion of the raw coal. If successful, the SRC process will permit the use of high sulfur coals as a boiler fuel, which otherwise could not be used under EPA regulations. This research program seeks to improve the economic attractiveness of the SRC process through the application of chemical engineering techniques.

Objective:

The objective of this research program is to systematically investigate, characterize, and delineate the effects of changes in process operating conditions, equipment configuration, and nature of raw materials upon the kinetics, mechanism, and extent of coal dissolution, heteroatom removal, and hydrogenation in the SRC and closely related processes, for the purpose of providing an increased fundamental understanding of SRC process chemistry as well as guidelines and recommendations leading to economic and technical improvements in SRC technology. The program objectives are being carried out in cooperation with the Southern Services' SRC pilot plant operation at Wilsonville, Alabama, and with the Rust Engineering subsidiary of Wheelabrator-Frye, Inc.

The research program is divided into three major tasks with several sub-tasks within each area. An outline of the program by tasks and subtasks is presented on the following page.

Program Task Outline

Task 1. Mechanistic Studies of Coal Particle Dissolution

- A. Dissolution Behavior as a Function of Coal Characteristics
- B. Effect of Solvent Type and Gas Phase Composition on Particle Dissolution
- C. Direct Visual Observation of In-situ Particle Dissolution

Task 2. Catalysis by Coal Mineral Matter

- A. Process Variable and Kinetics
- B. Characterization of Coal Minerals
- C. Regeneration/Pretreatment of Coal Minerals and Residue
- D. Effect on Individual Species in Coal Liquefaction Products
- E. Continuous Reactor Studies

Task 3. Analytical Support

- A. Fourier Transform Infrared Spectroscopy of Coal and SRC
- B. Energy Dispersive X-Ray Fluorescence of Coal and SRC

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SUMMARY

The concentration of hydroaromatics in a coal liquefaction solvent is regarded as a significant factor in the determination of solvent quality. An analytical method is described based on catalytic solvent dehydrogenation (CSD) for the measurement of transferable hydrogen, including hydroaromatic sources, in a solvent.

The dehydrogenation of several model compounds in the presence of Pd/CaCO₃ was conducted under batch conditions. Hydroaromatics containing six-member rings were found to dehydrogenate effectively. Lesser degrees of dehydrogenation were found for alkyl-substituted aromatics and saturated compounds. Material losses possibly related to coking and/or condensation reactions were found in the CSD of acenaphthene.

CSD was applied to a series of hydrogenated creosote oils plus several light recycle oils. The normalized H₂ volumes obtained by CSD could be correlated with the coal-dissolution ability of the creosote oils. It was not possible to include the light recycle oils in the same correlation.

¹³C-NMR was used to measure the transferable hydrogen of selected hydrogenated creosote oils and light recycle oils. Whole oils were used for the measurements. Values of transferable hydrogen determined by ¹³C-NMR were generally larger than the corresponding values obtained by

CSD. A smooth correlation was found between coal conversion and transferable hydrogen as measured by ^{13}C -NMR. The light recycle oils could not be fitted to the curve defined by the creosote oils.

Minerals indigenous to coal provide an internal but weak source of catalytic activity during liquefaction reactions. A sensitive probe reaction, cyclohexene hydrogenation/isomerization, was used to compare the catalytic activity of several clay minerals, oxides used as catalyst supports, pyrite and liquefaction residue ashes.

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I. INTRODUCTION

During the decade of the 70's, there developed within the United States a desire to secure alternative sources of liquid hydrocarbon feedstocks other than petroleum. The production of liquid hydrocarbons from coal has received considerable attention from the chemical and refining industries.

Coal is basically a hydrocarbon material, but the hydrogen to carbon (H/C) ratio of coal is much lower than the H/C ratio of petroleum. Typical values of the H/C ratio for coal are between 0.3 and 0.8 (1), while the H/C ratio of petroleum crudes are as large as 1.8. Coal liquefaction is essentially a process of increasing the H/C ratio of the coal, plus lowering its mineral and heteroatom (principally S, O and N) contents.

The first effective coal liquefaction process was that of Bergius (2) developed in Germany during the 1920's. For bituminous coals, slurries of pulverized coal and process oil were reacted with hydrogen gas at temperatures between 475-485°C and pressures in the range of 5000-10,000 psi. It is now recognized that such extremes of temperature and pressure mitigate against the most efficient transfer of hydrogen to the coal by tending to overhydrogenate the solvent (3).

Current research in coal liquefaction as represented by the H-Coal, Exxon Donor Solvent (EDS) and Solvent Refined Coal-II (SRC-II) processes

operate at temperatures between 425-465°C and pressures of 1500-2500 psi (4). Such conditions more nearly optimize the mechanism of hydrogen transfer from the gas phase to the coal via the solvent (donor solvent) versus the mechanism of direct transfer of molecular hydrogen to the coal. As discussed in Chapter II, a donor solvent contains chemically-bound hydrogen which can be readily transferred to coal fragments during the process of liquefaction. The chemically-bound hydrogen is primarily in the form of hydroaromatic compounds (3).

The first major objective of this work is to define a new analytical method which can be used to monitor the concentration of hydroaromatics in a coal liquefaction solvent. The method is catalytic solvent dehydrogenation (CSD).

The second major objective of this work is to develop and use the cyclohexene hydrogenation/isomerization system as a probe reaction to aid in the evaluation of the relative importance of various minerals having weak catalytic activity which might be contained in coal.

Several investigators have reported that minerals indigenous to coal catalyze coal conversion processes (5,6). In model compound studies, minerals such as pyrite and SRC residue ash have been shown to enhance hydrogenation and hydrodesulfurization reactions. In a coal liquefaction process such as SRC-II, the catalytic activity of the coal minerals may be particularly important since no external catalyst is added to the process (4).

II. THE MEASUREMENT OF HYDROAROMATICITY BY CATALYTIC DEHYDROGENATION

Introduction

Coal liquefaction at elevated temperatures is typically regarded as proceeding by a free-radical mechanism (7,8). Under this model, large coal molecules are viewed as forming free-radical fragments which can then be stabilized by the transfer of hydrogen atoms from solvent molecules. The donation of hydrogen to the coal free radicals prevents their recombination to form high molecular weight material of low solubility. An important characteristic of an effective coal liquefaction solvent is the ability of the solvent to transfer hydrogen to the coal, that is, function as a donor solvent. Additionally, it is desirable that the solvent be able to replenish the supply of donor molecules by the transfer of hydrogen from the gas phase to hydrogen depleted species.

Hill et. al., (9) have shown that hydroaromatics such as tetralin are effective coal dissolution solvents. Figure 1 illustrates the process. Transfer of more labile hydrogen from the saturated ring of tetralin forms naphthalene (dihydronaphthalenes are also possible intermediates). Naphthalene can then undergo hydrogenation directly from the gas phase or at a catalytic site in the reactor to regenerate tetralin. The tetralin/naphthalene system can, thus, be viewed as a hydrogen-shuttle between the gas phase and the coal undergoing liquefaction.

Figure 1. Hypothetical Stabilization of Coal Fragment by Donor Solvent and Regeneration of Solvent

The standard organic reference by Fieser and Fieser (10) defines hydroaromatics as the products of the hydrogenation of aromatic compounds. Under this definition, 1,2-dihydronaphthalene, tetralin (1,2,3,4-tetrahydronaphthalene) and decalin (perhydronaphthalene) are all regarded as hydroaromatics. In typical literature of coal conversion, however, hydroaromatic compounds are regarded as the partially-hydrogenated products of aromatic hydrogenation reactions. Such a definition does not regard decalin as hydroaromatic. It is useful in coal liquefaction work to focus attention on the partially-hydrogenated aromatic compounds since experimentally it is found that these species are more effective coal-liquefaction solvents than either their fully-aromatic or fully-saturated counterparts (see Chapter III for example). This work will adopt the more restricted view of hydroaromatic compounds as partially-hydrogenated aromatics.

Literature Review

Several methods have been proposed to measure the hydroaromatic content of a coal liquefaction solvent. The most significant of these is the ^{13}C nuclear magnetic resonance (^{13}C -NMR) method of Seshadri et. al., (11). The method is based upon the observation that resonances for ^{13}C nuclei attached to hydroaromatic protons in model compounds generally lie in the range of 22-31 ppm versus tetramethylsilane (TMS). Since saturated hydrocarbons have resonances in the same region, it is generally necessary to remove them chromatographically prior to the ^{13}C -NMR analysis (12). An aromatic/hydroaromatic fraction is used for the actual ^{13}C -NMR work.

At best, the ^{13}C -method involves errors of about 10% in the estimation of the hydroaromatic-hydrogen content of a solvent due to the experimental difficulty of equalizing the relative nuclear Overhauser enhancement (NOE) that occurs for the secondary and tertiary carbons of a hydroaromatic molecule versus the quaternary carbons (13). Chromatographic isolation of the aromatic/hydroaromatic fraction prior to ^{13}C -NMR work also separates polar compounds into another fraction. The polar fraction, like the saturated fraction, is usually not included in the ^{13}C analysis. Aromatic compounds with alkyl substituents can also be a source of error with the ^{13}C -method; for example, the methyl carbons of 1,8-dimethylnaphthalene absorb at 26.0 ppm relative to TMS (13).

Mass spectrometry (MS) and gas chromatography/mass spectrometry (GC/MS) have been proposed as possible tools to measure solvent hydroaromaticity (14). The tremendous complexity of typical coal process solvents severely limits simple MS analysis to group type analysis. In a recent publication by Cronauer et. al., (15) it is noted that the group types are assigned a molecular formula based upon a weight distribution of observed molecular weights. These assigned molecular formulas can only be regarded as most probable ones; they are not unique. Thus, it is not possible to obtain an absolute measure of the fraction of hydrogen which comes from hydroaromatic sources by MS group type analysis.

GC/MS in theory offers an absolute method of determining hydroaromaticity. However, not even capillary GC columns can adequately

resolve the large number of components present in a coal solvent such as SRC-II (15). Also, it is not possible to elute the higher-boiling components of SRC-II by gas chromatography.

The reduction of benzophenone to diphenylmethane has also been suggested as a way to measure the effective hydrogen-donating ability of a coal liquefaction solvent (16,17). Both of the cited references present kinetically-limited data on the conversion of benzophenone in the presence of various model compounds, as well as, coal-derived solvents. The data, however, are not sufficient to estimate concentrations of hydrogen-donor species. The work by Jeng does involve some experiments where reaction times (12 hr) are long enough that it would be expected that total hydrogen donor content could be approximated. Tetralin gave a 93.8% conversion of benzophenone for a 12 hr reaction time, versus 13.7% benzophenone conversion for 1.5 hr. It was not possible though to correlate the data obtained on several coal-derived liquids for 12 hr runs.

Bockrath and Noceti (18) have recently described a method of measuring a hydrogen-donor index of a coal solvent which utilizes the hydrogen-scavenging ability of benzyl radicals. The benzyl radicals are produced in situ with the solvent at moderate temperatures (130-170°C) from dibenzylmercury or dibenzyl diazene. The formation of toluene versus bibenzyl is used to estimate a donor index for the solvent. Side reactions involving the benzyl radicals and solvent make it difficult to use the method to determine hydroaromaticity quantitatively.

The CSD method developed in this work is an extension of earlier catalytic dehydrogenation of solid coal by Wender and coworkers (19, 20). In their studies, coal was refluxed for 5 hr in the solvent phenanthradine at its boiling point ($\sim 370^{\circ}\text{C}$) in the presence of the catalyst Pd/CaCO_3 . The reflux apparatus was at atmospheric pressure during the reaction, and H_2 gas was collected in an attached gas buret as it formed. It was demonstrated with several model hydroaromatic compounds (all three and four ring systems) that the technique gave nearly quantitative dehydrogenation of the hydroaromatic hydrogens.

The method of Wender is well-suited for solid coals, but presents problems when applied to liquids. Namely, several potential hydrogen donors in solvents of interest to coal liquefaction studies have boiling points below that of phenanthradine. Examples are 1,2-dihydronaphthalene, tetralin and indan. Such compounds would be driven primarily into the vapor phase during reflux in phenanthradine and have little opportunity to contact the Pd catalyst. Lowering the reflux temperature is not a practical answer to the dilemma, because dehydrogenations of hydrocarbons are generally endothermic, and the reaction time needed for complete dehydrogenation will become prohibitively long.

Experimental

Method

The CSD reactions were run in a sealed microreactor (tubing bomb reactor) for a period of 4.00 hr. The microreactor (volume ≈ 46 ml) was charged with about 1.00 g of the solvent to be monitored for hydroaromatic content. In the case of model compound runs, the solvent was

a solution of some hydroaromatic (10-30 wt.%) or other compound dissolved in 1-methylnaphthalene. Such solutions should offer a reasonable, binary approximation to a coal process-solvent. Also, 0.3000 g of the catalyst, 5% Pd/CaCO₃, was added to the microreactor.

After charging of materials, the microreactor joints were carefully sealed using Copper Anti-Seize Compound (Jet-Lube, Inc.) on all ferrules plus the valve stem tip (Nupro fine metering valve, see Equipment section) and properly tightened.

The microreactor was attached to a tank of compressed N₂, pressurized to about 800 psig and purged of air three times by venting through a release valve for this purpose followed by repressurization. While still under pressure, the microreactor was leak-tested with Snoop Liquid Leak Detector (Nupro Co.) and removed from the N₂ tank in a pressurized condition. The microreactor was then leak-tested a second time by immersion in a tank of water.

Following leak-testing, the microreactor was vented to atmospheric pressure through the metering valve, the valve closed manually and then the bonnet on the valve tightened with a wrench about 1/8 turn. This last step usually insured that the valve stem was properly seated for the duration of the reaction.

Reactions were run at 390°C using a 600 rpm agitation rate. Immediately after the allotted reaction time, the reaction was quenched by plunging the microreactor into cold water. Finally, the volume of any gas generated during the CSD process was measured by releasing the gaseous contents of the microreactor into a separate gas-measuring apparatus described in the Equipment section.

The technique of conducting the CSD reaction in a sealed reactor has the advantage over Wender's method of permitting light volatiles in a test solvent to contact the Pd catalyst. The CSD method has the disadvantage, though, that a moderate pressure is developed in the microreactor during the reaction. Since the extent of most dehydrogenation reactions of hydrocarbons are diminished by pressure, it is desirable to minimize the pressure.

Equipment

CSD experiments were run in microreactors made of 316 stainless steel. The body of the reactors were 3/4 inch O.D. with 0.065 inch wall thickness and 8 3/4 inches long. The reactor was closed on the bottom end by a Swagelok cap. Attached to the other end was a Nupro fine metering valve for gas handling. Connection of the valve to the reactor body was made through a 1/4 inch tube (3 1/2 inches long) and reducing unions. The resulting 46 ml volume of the microreactor coupled with the small reactant charge (1.00 g) tended to minimize pressure-buildup during the CSD reaction.

Reaction temperature was maintained by immersing the microreactor into a fluidized sand bath, Techne Inc. SBL 2D. The sand bath was regulated with a Techne TC4D temperature controller. The microreactor was agitated longitudinally in a vertical plane at 600 rpm, with a 1 1/2 inch stroke, by a variable speed motor equipped with crankshaft, bushing, couplings and an extension rod. See Figure 2 for a diagram of the apparatus.

Figure 2. Diagram of Reactor System

A schematic representation of the apparatus used for measuring the gas volume after CSD reaction is shown in Figure 3. The micro-reactor was connected by a short section of rubber tubing to the Hg-filled gas buret through a four-way stopcock. A monitor buret open to the atmosphere served as a convenient marker of Hg level in the adjustable Hg leveling-bulb. A sliding level indicator was provided to aid in reading Hg levels.

When using the gas-measuring apparatus, the Hg levels in the two burets must first be equalized at some upper position after attaching the microreactor. The four-way stopcock was usually used at this point to release the slight pressure that developed in the rubber tubing from the attachment process. After reading the Hg level with the stopcock interconnecting the microreactor and the gas buret, the Hg leveling-bulb was lowered to some arbitrary position. The air (or N_2) trapped in the gas buret was depressurized by this maneuver, making it possible to check for leaks in the apparatus by noting whether the Hg level in the gas buret stabilized at some position above the Hg level in the monitor buret. Then the metering valve on the microreactor was slowly opened, the gas contents of the reactor allowed to equilibrate with the contents of the gas buret and finally the leveling bulb adjusted to equalize the Hg levels in the two burets. The released gas volume was taken as the difference between the final and initial gas buret readings. Several minutes were always allowed for the temperature of the released gas to equilibrate with its surroundings. Temperature and barometric readings were taken to correct the observed gas volume to standard conditions.

Figure 3. Diagram of Gas-Measuring Apparatus

Samples for gas analysis by GC were readily obtained by connecting a rubber tubing with attached release valve and rubber septum to one of the unused arms of the stopcock.

Varian gas chromatographs (Models 920 and 1800, both with TC detection) were used for analysis of gas samples. Liquid products were analyzed on a Varian Model 3700 GC with FI detection. Usually, analyses involving two-ring or smaller aromatic compounds were performed with a 50 m, glass, SCOT, capillary column (Scientific Glass Eng.) coated with Apiezon-L. Three-ring and larger aromatic compounds were analyzed on a 10 ft column packed with 3% SP-2250 on 100-200 U.S. mesh Supelcoport (Supelco, Inc.). GC conditions are listed in Appendix B. A Varian CDS 111 microprocessor was attached to the output of all the gas chromatographs.

Catalyst surface area was determined by N_2 adsorption on an apparatus constructed in this laboratory (21).

Materials

The catalyst used in the CSD experiments was 5 wt % Pd supported on $CaCO_3$ and supplied by Aldrich. The surface area as determined by N_2 adsorption was $7.8 \text{ m}^2/\text{g}$. GC analysis of 1-methylnaphthalene (Aldrich, 97%) confirmed it to be 99.19% pure. Nitrogen gas (99.995%) was obtained from Alabama Oxygen Co.

Table 1 gives the sources and purities of all model compounds used in the CSD work. The purities were determined by GC analysis. The hexahydropyrenes were supplied by API-PSU Hydrocarbon Bank of The Pennsylvania State University.

Table 1. Model Compound Sources and Purities

Compound	Source	Purity by GC, %
1,2-Dihydronaphthalene	Aldrich, Tech.	98.01
1,4-Dihydronaphthalene	Pfaltz & Bauer	92.89
Tetralin	Aldrich	96.50
9,10-Dihydrophenanthrene	Aldrich, 98%	99.43
9,10-Dihydroanthracene	Aldrich, 98%	96.34
1,2,3,4,5,6,7,8-Octahydroanthracene	Alfred Bader	99.06
1,2,2a,3,4,5-Hexahdropyrene	Penn. State Univ.	95.34
1-n-Decyl-3,4,5,8,9,10-Hexahdropyrene	Penn. State Univ.	82.54
Acenaphthene	J. T. Baker	99.30
1,2,3,4-Tetrahydroquinoline	Aldrich, 97%	99.94
Ethylbenzene	Aldrich, 99%	97.55
Indan	Aldrich, 97%	98.11
Decalin	Aldrich	99.73
Hexadecane	Pfaltz & Bauer	99.63
Fluorene	Eastman, Tech.	99.11
O-Cresol	Fisher, Pur.	99.98
β -Naphthol	Mallincrodt, Pur.	99.52

Results and Discussion

General

The model compound CSD results are shown in Table 2. Hydrogen yields are calculated on the basis of formation of a completely conjugated product in all cases. A completely conjugated product is one having a maximum number of double bonds alternated with single bonds. While the dehydrogenation of a saturated compound such as hexadecane probably would not yield totally conjugated products only, this type of calculation basis puts the saturated compounds on an equal footing with the partially saturated hydroaromatics in the sense that the same weight is given to hydrogens derived from an alkyl or a partially aromatic source. Appendix A gives the structural formulas and names of the model compounds used, as well as, their most likely dehydrogenation products.

All experiments were run in duplicate, and the errors shown in Table 2 are 1/2 the range values. The model compound purities (Table 1) are incorporated in the H₂ yield calculations.

For convenience in analysis, the model compounds of Table 2 have been divided into three classes on the basis of their hydrogen yields: model donors, model weak donors and model nondonors. The model donors include all the hydroaromatics plus the heterocyclic compound, 1,2,3,4-tetrahydroquinoline. The weak donors include ethylbenzene, indan and the saturated compounds, decalin and hexadecane. The nondonors are fluorene, o-cresol and β -naphthol.

Under the CSD reaction, the model donors evolved a volume of H₂ considerably larger than that of a 1-methylnaphthalene (MN) blank.

Table 2. Model Compound Dehydrogenations

Compound	Calculation Basis, moles H ₂ /mole HA	H ₂ Yield, %
Donors		
1,2-Dihydronaphthalene	1	90.9 ± 0.8
1,4-Dihydronaphthalene	1	90.0 ± 0.3
Tetralin	2	89.9 ± 3.9
9,10-Dihydrophenanthrene	1	101 ± 3
9,10-Dihydroanthracene	1	99.7 ± 0.3
1,2,3,4,5,6,7,8-Octahydro- anthracene	4	102 ± 3
1,2,2a,3,4,5-Hexahdropyrene	3	90.1 ± 1.2
1-n-Decyl-3,4,5,8,9,10- Hexahdropyrene	8	60.9 ± 1.9
1,2,3,4-Tetrahydro- quinoline	2	96.1 ± 3.6

Table 2, continued

Compound	Calculation Basis, moles H ₂ /mole HA	H ₂ Yield, %
Weak Donors		
Ethylbenzene	1	38.5 ± 2.0
Indan	1	43.3 ± 0.6
Decalin	5	18.5 ± 3.9
Hexadecane	8	11.9 ± 2.0
Nondonors		
Fluorene		~0
o-Cresol		~0
β-Naphthol		~0
Acenaphthene		*

*No significant dehydrogenation product was observed in the CSD of acenaphthene, but the evolved H₂ volume was greater than a solvent blank.

(See MN section for data.) H_2 evolution with the model nondonors was within experimental error the same as a MN blank. The H_2 evolution of a weak donor was intermediate between these two extremes.

GC analysis was performed on the liquid products of all model compound CSD reactions. In the case of a model donor, the chromatogram was dominated by a peak corresponding to the completely aromatic derivative of the compound being dehydrogenated. Chromatograms of nondonors showed no evidence of reaction products.

It was assumed in the H_2 yield calculations for the model donors and the model weak donors that all collected H_2 came from the model compound only; that is, no attempt was made to correct for H_2 evolution from the 1-methylnaphthalene solvent. It is felt that this assumption over-estimates the H_2 yield for the model donors by less than 10% (see section on MN).

In all cases the product solutions of CSD runs were darkly colored while the reactants were usually colorless or only slightly colored. The possibility of condensation reactions (polymerization) among the reactants including the MN cannot be discounted. This matter is discussed further in the section on acenaphthene.

The gas collected from the CSD runs was analyzed by GC. In all cases, the evolved gas was found to be $\geq 99.9\%$ pure H_2 .

1-Methylnaphthalene (MN)

Neat 1-methylnaphthalene (MN) was found to undergo catalytic dehydrogenation. Presumably the dehydrogenation occurs through dimerization and similar higher-order reactions. (See Ref. (10) for a description

of a catalytic dehydrogenation reaction of benzene to biphenyl.) For an initially pure N_2 atmosphere, the extent of dehydrogenation was 12.2 mole % based on the H_2 gas collected and assuming MN dimerization with one mole of H_2 released for every mole of dimer formed. Several unidentified peaks ($< 1\%$) were seen in the chromatogram of dehydrogenated MN. However, a peak of the intensity expected of a dimer product could not be found. It is possible that a dimer product would not elute.

In spite of the ability of MN to undergo CSD, there frequently was good agreement for the model donors between the H_2 yield and the product yield as calculated from peak areas of the liquid product chromatograms. For example, the H_2 yield of 9,10-dihydrophenanthrene was $101 \pm 3\%$, while the yield of phenanthrene from the GC peak ratios was $99.5 \pm 0.5\%$.

The above observations suggest that in the presence of a hydroaromatic compound, the catalytic dehydrogenation of MN is suppressed. To test this hypothesis, a series of MN dehydrogenations were conducted in mixtures of H_2 and N_2 where the initial H_2 mole fraction was known, and the initial total pressure was 1 atm. The results are shown in Figure 4. MN dehydrogenation decreases monotonically from 12.2% for a final H_2 mole fraction of 0.20 (0.0 initial H_2 mole fraction) to 0.6% for a final H_2 mole fraction of 1.0, where the MN is assumed to dimerize and the extent of dehydrogenation is calculated from the volume of evolved H_2 .

Thermodynamically it is expected that the dehydrogenation of MN would be suppressed by the presence of a second compound capable of

Figure 4. Dehydrogenation of 1-Methylnaphthalene vs. Final H₂ Mole Fraction in H₂/N₂ Atmosphere

undergoing CSD. If the second compound is a hydroaromatic with a sufficiently large equilibrium constant for dehydrogenation relative to that of MN, the CSD of MN will be suppressed to the greater extent.

In typical CSD runs of model donors the volume of generated H_2 was at least 30 ml for a H_2 mole fraction of 0.39. From Figure 4, such a condition (assuming 0.9 g of MN) would imply that the MN contribution to the total H_2 volume would be at most 3 ml. Thus, it is reasoned that the H_2 yields of Table 2 may be overestimated by 10% or less for the model donors. Frequently, the volume of H_2 generated with model donors was greater than 30 ml, which depressed the dehydrogenation of MN to an even greater extent.

The volume of H_2 generated by a MN blank was about 10 ml, and the volume of H_2 generated by weak model donors was intermediate between a blank value and 30 ml. Since the MN dehydrogenation reaction will not be suppressed to the same degree for the model weak donors as it is for the model donors, the H_2 yields of model weak donors may be overestimated by more than 10%.

1,2-Dihydronaphthalene, 1,4-Dihydronaphthalene and Tetralin

The only observed product of 1,2-dihydronaphthalene, 1,4-dihydronaphthalene and tetralin CSD was naphthalene. For 1,2-dihydronaphthalene and 1,4-dihydronaphthalene, no starting materials were detected among the products. In the case of tetralin, the GC peak area of the unreacted tetralin was about 3% of the peak area for naphthalene.

Wilson et. al., (22) have measured the equilibrium constant for the gas phase dehydrogenation of tetralin. The reaction is

If it is assumed that the CSD of tetralin is a gas phase reaction and MN as well as N_2 can be treated as inerts, it is shown in Appendix C that the equilibrium expression can be written as

$$K_p = \frac{4\theta^3 p^2}{(1-\theta)(1 + 2\theta + r)^2}$$

In the above,

θ = degree of tetralin dehydrogenation,

and

$$r = \frac{\text{moles of inerts}}{\text{initial moles of tetralin}}$$

K_p is the equilibrium constant and P is the total pressure. Assuming ideality for the gas where n_i = initial moles of tetralin, T = temperature, V = volume, and R = ideal gas constant:

$$P = n_T (1 + 2\theta + r) \frac{RT}{V}$$

Applying the data of Wilson et. al., at the CSD temperature, 390°C , one obtains for a 10 wt % tetralin solution in MN

$$\theta = 0.9917$$

$$P = 12.32 \text{ atm}$$

The quantity θ corresponds to the previously defined hydrogen yield, which for tetralin was $89.9 \pm 3.9\%$.

A higher level of tetralin conversion was found with a $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst (Shell 324). The results are given in Figure 5. Tetralin was dehydrogenated as a function of time and found to achieve a hydrogen yield of 99.0% after 4.0 hr reaction time.

The H_2 yield for tetralin using Pd/CaCO_3 is regarded as adequate. Further CSD work with the Shell 324 Catalyst was not pursued because alumina-supported catalysts frequently give rise to hydrocracking reactions (23). Also, it was felt that the Shell catalyst could be too powerful a dehydrogenation catalyst; that is, dehydrogenation of saturates might be a greater problem with the NiMo catalyst than Pd.

9,10-Dihydrophenanthrene

Only phenanthrene was detected in the GC analysis of the 9,10-dihydrophenanthrene CSD products. The peak area of unreacted 9,10-dihydrophenanthrene was less than 1% of the peak area of phenanthrene.

9,10-Dihydroanthracene and 1,2,3,4,5,6,7,8-Octahydroanthracene

GC analysis of 9,10-dihydroanthracene CSD products indicated quantitative conversion to anthracene; no unreacted 9,10-dihydroanthracene was detected. The analysis of 1,2,3,4,5,6,7,8-octahydroanthracene (OHA) revealed anthracene as the predominant dehydrogenation

Figure 5. Tetralin Conversion Measured by H₂ Evolution as Function of Time (Shell 324)

product. Two other products were noted: the first was identified as 9,10-dihydroanthracene (peak area about 8% of the anthracene peak); the second product (peak area about 4% of anthracene) could not be identified. Based on the product's retention time, it may be another dihydro-product of anthracene, although other possibilities such as a structure with a five-member ring cannot be discounted. No OHA was detected in the products.

1,2,2a,3,4,5-Hexahdropyrene and
1-n-Decyl-3,4,5,8,9,10-Hexahdropyrene

The dominant product for the CSD of 1,2,2a,3,4,5-hexahdropyrene (HHP) was pyrene (> 95% peak intensity). Two additional products of nearly equal peak intensity were observed but not identified. No HHP was observed.

The hydrogen yield of 1-n-decyl-3,4,5,8,9,10-hexahdropyrene (DHHP) reported in Table 2 is based upon dehydrogenation of the alkyl sidechain, as well as, the condensed rings to form a completely conjugated product. For complete dehydrogenation as described, the H_2 yield was $60.9 \pm 1.9\%$. If one assumes dehydrogenation of the ring system only, the H_2 yield becomes $162 \pm 5\%$. Assuming that the DHHP rings were dehydrogenated to the same degree as HHP (H_2 yield = $90.1 \pm 1.2\%$), the results indicate significant dehydrogenation of the decyl group. Sidechain dehydrogenation also was observed with ethylbenzene.

At least 9 different peaks were observed in the product chromatogram of a DHHP dehydrogenation. The peaks were of comparable intensity; none of them could be identified due to a lack of appropriate standards for spiking the chromatogram. Unreacted DHHP was not observed in the product slate.

1,2,3,4-Tetrahydroquinoline (THQ)

The only observed product of THQ dehydrogenation was quinoline. No THQ was detected in the GC analysis of the liquid product.

THQ has been reported to be an excellent hydrogen donor in coal liquefaction (18). THQ and quinoline have also been noted to be catalyst poisons for some processes (23). The near quantitative dehydrogenation of THQ found in this work suggests that poisoning of the Pd catalyst by nitrogen heterocycles may not be a problem in CSD.

Ethylbenzene and Indan

The H_2 yield reported for ethylbenzene was computed on the basis of a possible loss of 1 mole of H_2 per mole of ethylbenzene; that is, styrene was expected to be the primary product. A trace of styrene (< 1%) was detected in the GC analysis of the products of ethylbenzene CSD. Given the propensity of styrene to polymerize even at room temperature (10), it may not be unreasonable that so little styrene was detected.

The only significant product found in the GC analysis of indan CSD was indene. The peak area of indene was about 30% of the indan peak. The moderate degree of dehydrogenation found (H_2 yield = $43.3 \pm 0.6\%$) is consistent with the general observation that saturated, five-member ring structures are poor hydrogen donors in coal liquefaction (15).

Decalin and Hexadecane

As saturated compounds, both decalin and hexadecane are expected to be poor hydrogen donors in coal liquefaction (see Chapter III).

GC analysis of the CSD products of decalin revealed tetralin and naphthalene. The peak ratio of naphthalene to tetralin was about 50 to 1. Neither 1,2-dihydronaphthalene nor 1,4-dihydronaphthalene was detected. Given that the two dihydronaphthalenes, as well as, tetralin were found to readily dehydrogenate (Table 2), it is reasonable that they would be fairly reactive intermediates in the conversion of decalin to naphthalene.

H₂ yields of all the compounds of Table 2 have been calculated on the basis of complete dehydrogenation to form a totally conjugated product. The formation of naphthalene as the chief product of decalin CSD is consistent with the assumed calculation basis.

Dehydrogenation of hexadecane yielded eight resolvable components other than hexadecane in the GC output. The largest of the peaks was 1.2% of the hexadecane peak. As with the case of 1-n-decyl-3,4,5,8,9,10-hexahdropyrene, a large number of products might be formed from the CSD of hexadecane.

Fluorene, o-Cresol and β -Naphthol

CSD of fluorene, o-cresol and β -naphthol gave hydrogen volumes experimentally the same as that of a MN blank. For all three compounds, there was no product in the GC chromatogram but the unreacted starting material. The compounds have been accordingly classified as nondonors, and their H₂ yields have been taken to be zero with the evolved H₂ assumed to come from MN.

Wender and coworkers (24) have reported a H₂ yield of 39% for dehydrogenation of fluorene in phenanthradine under atmospheric reflux

conditions. They also state that some MS evidence was obtained for 9,9'-difluorenyl (a dimer of fluorene) among the products. The possibility of fluorene dimers forming under the conditions of this work cannot be discounted; it would be difficult to elute difluorenyl from the GC columns used, and only fluorene was observed in the product chromatograms. However, if all the H_2 evolved in these experiments were assumed to come from fluorene dimerization (1 mole H_2 /2 mole fluorene) rather than from the dimerization of MN, it would require complete reaction of the fluorene, and no fluorene would be observed in the products.

Wender et. al., also observed significant hydrogen yields for the dehydrogenations of 4-hydroxydiphenyl (72%) and 4,4'-dihydroxydiphenyl (94%). Dehydrogenation at atmospheric pressure in an open system such as employed by Wender would be expected to more effectively dehydrogenate compounds than the conditions employed in this work, since there is no buildup of H_2 pressure in an open system.

Acenaphthene

Acenaphthene (ACN) contains a partially saturated, five-member ring and is not generally regarded as an effective hydrogen donor in coal liquefaction (11). The expected dehydrogenation product of ACN is acenaphthylene; a reaction which involves removal of 1 mole of H_2 per mole of ACN.

GC analysis of the reaction products indicated the acenaphthylene peak intensity was less than 1.1% of the ACN peak. No other significant reaction products were detected.

The H_2 evolution from the CSD of acenaphthene, however, was significantly above that of a MN blank. In fact, if the H_2 yield is calculated on the basis of ACN losing 1 mole of H_2 per mole of reactant and all the H_2 is assumed to come from ACN, the H_2 yield = $99.7 \pm 3.1\%$, indicating nearly total conversion of acenaphthene.

To help resolve the discrepancy between the GC results and the apparent H_2 yield, a material balance was performed on the reaction products of acenaphthene CSD. An aliquot of the liquid products was analyzed on the GC using the internal standard method. THF (Burdick & Jackson) was used as the internal standard. The results indicate a $12.4 \pm 1.4\%$ loss of 1-methylnaphthalene and a $26.7 \pm 3.3\%$ loss of acenaphthene. Assuming that the unrecovered MN involves a dimerization process to yield 1 mole H_2 /2 mole MN and the unrecovered ACN represents a simple dehydrogenation to yield 1 mole H_2 /1 mole ACN, the predicted H_2 evolution is only 74.8% of the observed H_2 volume. The results imply more complex stoichiometric relations than assumed.

It appears that ACN and MN are undergoing conversion processes to substances that are not eluting from the GC column. In Chapter VI, the material loss of cyclohexene and its products in the presence of various mineral catalysts under hydrogenation conditions is discussed. With one of the minerals, kaolinite, it is shown that cyclohexene or its products undergo chemisorption and conversion into higher molecular weight components on the surface of the kaolinite. CSD of acenaphthene plus the other model compounds studied yielded dark solutions that could be the result of coking or polymerization reactions. Also, the Pd

catalyst was always converted from a light gray material to a nearly black product during CSD; this also suggests coking.

It is possible that under CSD conditions acenaphthene, as well as, 1-methylnaphthalene participate in condensation reactions that generate more than 1 mole of H_2 for every 2 moles of reactants condensing.

Wender et. al., (24) reported a hydrogen yield of 29% for the dehydrogenation of acenaphthene under their conditions. They could find no evidence of acenaphthylene product by either MS or UV analysis. They did observe in the mass spectrum of the products some indication of a compound having a mass corresponding to a dimer of acenaphthene.

Because of the inability to clarify the source of the H_2 produced in the CSD of ACN, a hydrogen yield is not estimated for it in Table 2.

Conclusions

The studied model hydroaromatics (including 1,2,3,4-tetrahydroquinoline) containing six-member rings dehydrogenate effectively under the CSD conditions. No significant hydrocarbon products are observed in the gas phase.

Alkyl sidechains attached to aromatic rings may also dehydrogenate under the CSD method but not to the same degree as hydroaromatic rings for the compounds studied.

Dehydrogenation of saturated compounds, while less significant than alkyl substituents on aromatic rings, may necessitate their removal by some chromatographic method (25) prior to application of CSD to coal process-solvents.

The observation of material losses in the CSD of acenaphthene/1-methylnaphthalene casts an uncertainty over whether observed H_2 yields can actually be regarded as quantitative measures of hydroaromaticity. It may be best to view the CSD technique as a possible solvent quality index.

III. PREPARATION OF HYDROGENATED CREOSOTE OILS

Introduction

A series of creosote oils hydrogenated to different degrees were prepared to provide a systematic group of coal liquefaction solvents which together with three light recycle oils (LRO) plus four model compound solvents might be used to evaluate the CSD method of hydro-aromaticity determination versus other methods (11,14,16). The coal dissolution ability of all the solvents were determined in batch liquefaction experiments and correlated with their elemental hydrogen content. This work follows closely that described by Jeng (17).

Experimental

Equipment

Hydrogenations were performed in a 300 ml magne-drive autoclave from Autoclave Engineers, Inc.. Carbon, hydrogen and nitrogen (CHN) analysis of all the solvents was done on a Perkin Elmer 240 Elemental Analyzer. Catalyst presulfiding was done with a Lindberg furnace.

Materials

The creosote oil was furnished by Southern Company Services, Inc.. The creosote oil was originally from Allied Chemical Co. (24-CB). The hydrogenation catalyst, $\text{CoMo/Al}_2\text{O}_3$, came from Harshaw Chemical Co.. Hydrogen gas used was Linde, 99.995% purity.

Identification codes and origins of the light recycle oils were: LRO-1, Kentucky #9 (Lafayette); LRO-2, Western Kentucky; LRO-3, Indiana V.

Model compound solvents were 1-methylnaphthalene (Aldrich, 97%), tetralin (Aldrich) and decalin (Aldrich). Also, a "Mobil synthetic solvent" (26) was used. Its composition (wt %) was: 2% 4-picoline (Aldrich, 98%), 17% cresol (Baker, pur.), 43% tetralin, 38% 1-methylnaphthalene.

In the coal dissolution experiments, the coal was W. Ky. 9/14, - 20 + 270 US mesh. Cresol (Baker, pur.) extraction was used to estimate the dissolution yields; tetrahydrofuran (THF) was Baker grade.

Methods

The CoMo/Al₂O₃ (5.00 g) was presulfided at 400°C, with 100 ml/min 10 vol % H₂S in H₂, for 2 hr (27). The catalyst was contained in a porcelain boat and placed within a preheated tube furnace.

Eight different creosote oils, including one dehydrogenated oil, were prepared in autoclave runs. A summary of reaction conditions for the hydrogenations is given in Table 3. The listed reaction times do not include heatup time (~ 20 min) or quenching time (~ 2 min in ice water). All coal liquefaction solvents were stored under N₂ (28).

Coal dissolution experiments were conducted in 316 stainless steel microreactors constructed of 1/2 inch O.D. tubing, 6 inches long and 0.035 inch wall thickness. The reactor ends were sealed with Swagelok caps; no valve was used. Internal reactor volume was about 13 ml. The reactor was used on the same shaking apparatus shown in Figure 2.

Table 3. Reaction Conditions for Hydrogenation of Creosote Oil

Reaction Condition	CO-0*	CO-1(900)	CO-1	CO-3	CO-6	CO-12	CO-24	CO-48†
Creosote Oil (g)	150	150	150	150	150	150	150	150
Sulfided Co-Mo/Al ₂ O ₃ (g)	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00(10.0)
Temp (°C)	370	370	370	370	370	370	370	370
Stirring Rate (rpm)	1000	1000	1000	1000	1000	1000	1000	1000
Pressure (psig)**	1800	900	1800	1800	1800	1800	1800	2400(3000)
Time (hr)	6.00	1.00	1.00	3.00	6.00	12.00	24.0	24(24)

*N₂ substituted for H₂.

†Quantities in parentheses refer to a second 24 hr reaction period.

**Repressurized with H₂ every hour.

Reaction conditions were the same as those established by Jeng (17): 2.500 g coal, 5.000 g solvent, 1 atm air (initially), 410°C, 30.0 min, 860 rpm. No catalyst and no H₂ were used.

Following the dissolution experiment, the dissolution yield was determined by cresol extraction for each solvent. 70 ml of cresol was heated to boiling and then used to wash the contents of a microreactor into a beaker. The resulting mixture was then heated for several minutes to boiling and vacuum filtered through a Whatman #50 hardened filter paper. The filter cake was then washed with an additional 60 ml of hot cresol, followed by sufficient tetrahydrofuran (~ 50 ml) to yield a clear filtrate. Ashing of the dried filter cake was used to finally calculate the dissolution yield (17).

Results and Discussion

Hydrogen content (Table 4) of the creosote oils varied from a low of 6.29% for the dehydrogenated oil (CO-φ) to a high of 10.74% for the 48 hr hydrogenated oil (CO-48). The relative constancy of the carbon content (~ 90%) for all the oils suggests that the hydrogenation process is not simply an addition of hydrogen but heteroatom removal as well.

Table 5 summarizes the dissolution yields measured for all the solvents examined, and Figure 6 presents a correlation between the dissolution yield and the hydrogen content of the solvents.

Results nearly identical to those of Figure 6 were found by Jeng (17). A smooth curve can be drawn through the creosote oil points having a maximum at about 8.5% hydrogen. LRO dissolution yields are

Table 4. Carbon, Hydrogen and Nitrogen Contents of Solvents

Solvent	H, Wt %	C, Wt %	N, Wt %
Creosote Oil	6.38 ± 0.01	90.71 ± 0.17	1.17 ± 0.04
CO-0	6.29 ± 0.05	90.96 ± 0.08	0.79 ± 0.02
CO-1(900)	6.67 ± 0.11	90.56 ± 0.56	1.12 ± 0.32
CO-1	6.84 ± 0.07	90.81 ± 0.06	1.06 ± 0.09
CO-3	7.20 ± 0.18	90.56 ± 0.71	1.18 ± 0.38
CO-6	7.45 ± 0.10	90.59 ± 0.16	0.59 ± 0.03
CO-12	8.14 ± 0.09	90.35 ± 0.16	0.44 ± 0.05
CO-24	8.59 ± 0.18	89.37 ± 1.10	0.53 ± 0.35
CO-48	10.74 ± 0.11	89.13 ± 0.15	~ 0.00
LR0-1	8.45 ± 0.12	87.38 ± 0.08	0.74 ± 0.05
LR0-2	8.36 ± 0.09	87.34 ± 0.06	0.30 ± 0.06
LR0-3	9.20 ± 0.08	86.35 ± 0.03	0.72 ± 0.01
1-Methylnaphthalene	7.40 ± 0.05 (7.09)	92.72 ± 0.10 (92.91)	0.22 ± 0.16 (0.00)
Mobil Synthetic	8.26 ± 0.10 (8.05)	89.15 ± 0.20 (89.14)	0.35 ± 0.05 (0.30)
Tetralin	9.35 ± 0.03 (9.15)	89.24 ± 0.11 (90.85)	0.04 ± 0.12 (0.00)
Decalin	13.44 ± 0.14 (13.12)	86.94 ± 0.13 (86.88)	0.12 ± 0.12 (0.00)

*Quantities in parentheses are theoretical values.

Table 5. Dissolution Yields by Cresol Extraction for W. Ky. 9/14 Coal

Solvent	Dissolution Yield (Wt %)
Creosote Oil	19.1 $\pm$ 2.5
CO-0	23.5 $\pm$ 1.3
CO-1(900)	38.0 $\pm$ 0.4
CO-1	54.5 $\pm$ 1.3
CO-3	61.9 $\pm$ 1.4
CO-6	74.0 $\pm$ 1.0
CO-12	82.6 $\pm$ 0.5
CO-24	86.4 $\pm$ 0.1
CO-48	70.2 $\pm$ 0.8
LRO-1	42.6 $\pm$ 2.0
LRO-2	46.1 $\pm$ 1.7
LRO-3	51.9 $\pm$ 0.7
1-Methylnaphthalene	17.1 $\pm$ 0.6
Mobil Synthetic	62.3 $\pm$ 1.7
Tetralin	71.8 $\pm$ 1.1
Decalin	25.5 $\pm$ 1.0

Figure 6. Coal Dissolution Yield Versus Hydrogen Content

consistently lower than those of creosote oils for the same hydrogen content. Tetralin lies near the maximum of the curve. Decalin and 1-methylnaphthalene have dissolution yields among the lowest observed. (Jeng did not report data on these two compounds.)

There is an optimal level of hydrogenation for the creosote oils in these experiments. Decalin, a saturated compound, appears to be over-hydrogenated for coal liquefaction; and 1-methylnaphthalene, an aromatic compound, appears to be under-hydrogenated. Tetralin, a hydroaromatic compound, seems a near-optimal solvent for coal liquefaction.

IV. CATALYTIC SOLVENT DEHYDROGENATION OF CREOSOTE OILS AND LIGHT RECYCLE OILS

Introduction

The method of catalytic solvent dehydrogenation (CSD) described in Chapter II was applied to the hydrogenated creosote oils, light recycle oils and the Mobil synthetic solvent described in Chapter III.

In the work of Jeng (3,17), several different experimental parameters were investigated to determine if it was possible to correlate the coal-dissolution ability of a large number of coal-derived solvents with any one of the measured parameters. The solvent-quality parameters studied included: hydrogen content, atomic C/H ratio, IR ratio, aromatic hydrogen, α hydrogen, β hydrogen, γ hydrogen, average chemical shift and degree of partial hydrogenation. The aromatic, α , β and γ hydrogen were determined by proton NMR. The degree of partial hydrogenation was defined in terms of the weight percentages of tetralin plus dihydronaphthalenes divided by the weight percentages of naphthalene, dihydronaphthalenes, tetralin plus decalin. The weight percentages of the various compounds were determined by GC.

Generally, Jeng found that relatively smooth correlations existed between coal conversions and any one of the examined parameters for the hydrogenated creosote oils. The recycle oils, however, could not be fitted to the curves defined by the creosote oils nor was it possible

to correlate the recycle oils among themselves. The results of Figure 6 illustrate the situation for a plot of coal conversion against hydrogen content for the solvents examined in this work.

It is of interest to determine if the CSD method can serve as a correlation parameter for coal conversion. Qualitatively, CSD results should yield some indication of the relative abundance of hydroaromatics and other possible hydrogen donors in a coal liquefaction solvent. The method is deficient in that dehydrogenation of alkyl side-chains and saturated species can occur. Also, condensation reactions (dimerization, etc.) make it difficult to interpret the results of CSD.

Ideally, CSD should be applied to a coal solvent fraction after removal of saturates. Some preliminary results are given on the application of CSD to aromatic/hydroaromatic fractions of creosote oil and CO-24 (Table 3). All other dehydrogenation results refer to the whole liquid.

Experimental

The microreactors, agitators and gas-measuring apparatus are described in Chapter II. The catalyst, Pd/CaCO_3 , was the same as used in the model compound runs. Solvents used for the dehydrogenations are described in Chapter III.

Reaction conditions were: 390°C , 4.00 hr, 600 rpm, N_2 atmosphere (1.0 atm, initially), 0.3000 g 5% Pd/CaCO_3 . The quantity of test solvent was varied to restrict the volume of evolved H_2 to within about 25 to 65 ml at STP (Table 6). Limiting the volume of H_2 evolved prevented the pressure buildup during dehydrogenation from suppressing the

reaction to any greater extent than might have occurred in the model compound work. One series of experiments, using solvent CO-24 in sufficient quantity to generate 139 ml of H_2 served as a check on the importance of the pressure-limiting effect. These results are described below.

Results and Discussion

Results for the CSD of the hydrogenated creosote oils, light recycle oils and the Mobil synthetic solvent are presented in Table 6. The data have been normalized to one gram of reactant. The errors are one-half the range values. The evolved gas was determined to be $> 99\% H_2$ for all runs by GC analysis.

Solvent CO-24, the solvent with the highest coal dissolution yield (Table 5), was dehydrogenated at two different levels of solvent charge. At approximately 0.3 g charge of the solvent, the normalized H_2 volume (STP) was 149 ± 14 ml; at approximately 1.0 g charge, the normalized H_2 volume equaled 132 ± 7 ml. The results suggest that dehydrogenation in this case was only mildly pressure-limited, if at all. Since CO-24 represents one of the more extreme examples of possible dehydrogenation, it is likely that equilibrium limitation was not a significant factor in the other CSD results. The similarity of the two values also suggests that the ratio of catalyst to solvent (catalyst loading) was not significant for the ratios studied. If the dehydrogenation reactions occurring during CSD were actually approaching equilibrium at the smaller catalyst loading (0.3 g catalyst/1.0 g solvent), then increasing

Table 6. Catalytic Solvent Dehydrogenation of Hydrogenated Creosote Oils and Light Recycle Oils

Solvent	Mass, g	H ₂ , ml @ STP	Normalized H ₂ [*] , ml @ STP	Ave. Norm. H ₂ , ml @ STP
CO-0	1.0017	24.1	24.1	24.0 ± 0.1
	1.0472	25.0	23.9	
Creosote Oil	1.0000	25.0	25.0	24.4 ± 0.5
	0.9955	23.5	23.6	
	0.9987	24.6	24.6	
CO-1(900)	0.9190	27.1	29.5	29.6 ± 0.1
	0.8256	24.5	29.7	
CO-1	0.8585	32.5	37.9	38.2 ± 0.3
	0.8505	32.7	38.5	
CO-3	0.8124	39.4	48.5	49.0 ± 0.7
	0.7977	39.8	49.9	
	0.8173	39.8	48.7	
CO-6	0.6002	43.0	71.7	64.4 ± 7.4
	0.6368	36.3	57.0	
CO-12	0.5275	55.4	105	106 ± 1
	0.5053	53.6	106	
CO-24	0.3124	42.2	135	149 ± 14
	0.3063	49.9	163	
(CO-24	0.9996	125	124	132 ± 7
	1.0033	139	139	
CO-48	0.4023	66.4	165	156 ± 10
	0.4380	63.9	146	

Table 6, continued

Solvent	Mass, g	H ₂ , ml @ STP	Normalized H ₂ [*] , ml @ STP	Ave. Norm. H ₂ , ml @ STP
LRO-1	0.6186	33.5	54.1	53.4 ± 0.7
	0.6101	32.2	52.8	
LRO-2	0.7832	54.6	69.7	74.2 ± 4.4
	0.6301	49.5	78.6	
LRO-3	0.6442	38.7	60.1	66.9 ± 5.3
	0.6235	44.1	70.7	
	0.6107	42.7	70.0	
Mobil	0.2797	38.0	136	132 ± 4
Synthetic	0.2864	36.4	127	

* Normalized to one gram of reactant.

the loading should not have been an important effect on the volume of evolved H_2 in the absence of coking.

The Mobil synthetic solvent (2% 4-picoline, 17% cresol, 43% tetralin and 38% 1-methylnaphthalene) gave nearly quantitative dehydrogenation on the basis of tetralin converting to naphthalene. The H_2 yield was $93.4 \pm 3.0\%$. This value compares favorably with the $89.9 \pm 3.9\%$ H_2 yield observed for CSD of tetralin/1-methylnaphthalene (Table 2).

In the model compound work, it was noted that catalyst poisoning did not appear to be a problem with the CSD of 1,2,3,4-tetrahydroquinoline. The ability of tetralin to effectively dehydrogenate in the presence of 4-picoline (4-methylpyridine) further suggests that catalyst poisoning by nitrogen heterocycles may not be a critical factor in CSD. These observations are reinforced by the work of Wender et. al., (19,20) where several model hydroaromatics were found to readily dehydrogenate in the presence of the solvent phenanthradine.

A plot of coal dissolution yields against normalized H_2 volumes (Figure 7) gives a fairly smooth correlation for the hydrogenated creosote oils. The light recycle oils and the Mobil solvent are less effective coal dissolution solvents than the creosote oils for a given normalized H_2 volume.

Figure 8 shows the relationship between hydrogen content of the solvents as determined by CHN analysis (Table 4) and normalized H_2 volumes. There is a smooth, monotonic increase in both H content and normalized H_2 volume when going from the dehydrogenated oil, CO- ϕ , to the 24 hr-hydrogenated oil, CO-24. However, the 48 hr-hydrogenated oil, CO-48, represents a sharp discontinuity on the plot. Its hydrogen

Figure 7. Coal Dissolution Yield vs. H₂ Volume by CSD for Normalized Solvent Quantities

Figure 8. Hydrogen Content vs. H₂ Volume by CSD for Normalized Solvent Quantities.

content is much greater than would be predicted on the basis of an extrapolation of the curve for the less hydrogenated oils. In terms of its coal dissolution ability (Figures 6 & 7), CO-48 is an over-hydrogenated solvent.

If it is assumed that the primary source of the normalized H_2 volume of the creosote oils is the CSD of hydroaromatics, the CO-48 discontinuity of Figure 8 may indicate a sharp increase in the proportion of saturates formed in the preparation of that oil versus the less vigorously hydrogenated oils.

Appendix D contains the calculated elemental compositions for a series of hydrogenated synthetic creosote oils. The oils are based upon the ten most abundant components of creosote oil as determined by GC/MS (29). All the components of the synthetic creosote oil are unsaturated two-or three-ring aromatic compounds (including two heterocycles). Elemental compositions (Table 26) are calculated for an unsaturated oil, an oil with all components having one six-membered ring saturated, an oil with all components having two six-membered rings saturated and a totally saturated oil. The hydrogen contents for the unsaturated, one-ring saturated, two-ring saturated and saturated oils are 6.35, 8.89, 12.33 and 12.76 wt %, respectively.

The experimental hydrogen content of creosote oil, 6.38 ± 0.01 wt % (Table 4), agrees quite well with the value of the unsaturated, synthetic creosote oil. The hydrogen contents of all the hydrogenated creosote oils between CO- ϕ and CO-24 lie below the one-ring saturated hydrogen content. The oil CO-48 has a hydrogen content (10.74 ± 0.11 wt %) between the one- and two-ring saturated values. Since creosote

oil is dominated by two-ring structures, the calculations imply a possible sharp increase in the concentration of saturates in CO-48 relative to the less hydrogenated oils.

The CHN data of Table 4 can be used to estimate the fraction of the total hydrogen in a solvent which can be removed by catalytic dehydrogenation. This quantity is defined as the % evolved H.

$$\text{Evolved H, \%} = \frac{10^4 (\text{Norm. H}_2 \text{ Vol. ml/g}) (2.0158 \text{ g/g-mole})}{(\text{H Content, wt \%}) (22,414 \text{ ml/g-mole})}$$

Where the released H_2 of CSD comes mostly from hydroaromatic compounds, the % evolved H of a solvent indicates the % hydroaromatic hydrogen.

Calculated values of % evolved H for the solvents studied are given in Table 7; a plot of coal dissolution yield versus % evolved H is shown in Figure 9. Coal dissolution is experimentally found to increase as the tetralin concentration increases of a tetralin/1-methylnaphthalene solution (30). Kuan observed that the dissolution of W. Ky. 9/14 coal as measured by THF solubles approached 70% for increasing tetralin concentrations. Thus, it is expected that a plot of coal dissolution as a function of concentration of hydroaromatics should give a smooth correlation. Normalized H_2 volume, the independent variable of Figure 7, is effectively a concentration quantity; it refers to the volume of H_2 catalytically evolved from one gram of a solvent. To the degree that the normalized evolved H_2 can be assumed to come from the hydroaromatics in a solvent, Figure 7 should be the preferred manner of plotting the data of CSD. The relatively smooth curve obtained when coal dissolution is plotted against %

Table 7. Percent Evolved H of Solvents

Solvent	Evolved H, %
C0-0	3.43 ± 0.03
Creosote Oil	3.44 ± 0.07
C0-1(900)	3.99 ± 0.08
C0-1	5.02 ± 0.09
C0-3	6.12 ± 0.24
C0-6	7.77 ± 1.00
C0-12	11.7 ± 0.2
C0-24	15.6 ± 1.8
C0-48	13.1 ± 1.0
LR0-1	5.68 ± 0.16
LR0-2	7.98 ± 0.59
LR0-3	6.54 ± 0.57
Mobil Synthetic	14.4 ± 0.6

Figure 9. Coal Dissolution Yield vs. % Evolved H

evolved H (Figure 9) is regarded as fortuitous; it is a result of the leveling effect that occurs when normalized H₂ volumes are divided by the hydrogen content of a solvent. What is significant is the % hydroaromatics in a solvent not the % hydroaromatics of the hydrogen content.

It is of particular interest to compare the results of CSD to the ¹³C-NMR results of Seshadri et. al., (11). Both of the methods attempt to measure the hydroaromatic content of a solvent. For this purpose, the transferable hydrogen defined by Seshadri is

$$\text{Transferable H, wt \%} = \frac{10^2 (\text{Norm. H}_2 \text{ Vol., ml/g}) (2.0158 \text{ g/g-mole})}{22,414 \text{ ml/g-mole}}$$

Table 8 summarizes the transferable H values for the solvents.

Seshadri et. al. reported values of transferable hydrogen ranging from 0.29 to 0.95 for seven different coal process-solvents. It is encouraging that the values of transferable H found in this work for the three LRO solvents are near the middle of the range observed by the ¹³C method. A direct comparison of the results of CSD with the measurement of hydroaromaticity by ¹³C-NMR for the same series of solvents would be desirable.

The saturated compounds, decalin and hexadecane, were found to undergo partial catalytic dehydrogenation in the model compound investigations (Table 2). Also, alkyl sidechains attached to aromatic rings were found to partially dehydrogenate. Ideally, saturates should be removed from a coal process solvent before applying the method of CSD.

Table 8. Transferable H of Solvents by CSD

Solvent	Transferable H, wt %
CO-0	0.216 ± 0.001
Creosote 011	0.219 ± 0.005
CO-1(900)	0.266 ± 0.001
CO-1	0.344 ± 0.002
CO-3	0.441 ± 0.006
CO-6	0.579 ± 0.067
CO-12	0.953 ± 0.009
CO-24	1.34 ± 0.13
CO-48	1.40 ± 0.09
LRO-1	0.480 ± 0.007
LRO-2	0.667 ± 0.040
LRO-3	0.602 ± 0.047
Mobil Synthetic	1.19 ± 0.03

Two of the solvents of this work, creosote oil and CO-24, were fractionated by high performance liquid chromatography (HPLC) to remove their saturated components (25). The chromatography method separates the original solvent into three fractions: saturates, aromatics/hydroaromatics and polars. CSD was then applied to the aromatic/hydroaromatic fractions (Table 9).

The aromatic fractions constituted 82.2 ± 0.8 and 88.8 ± 0.6 wt % of the original whole oils for creosote oil and CO-24, respectively.

The normalized H_2 volumes obtained for the two aromatic fractions were relatively close to their whole oil values. The results imply that it may not be necessary to remove the saturates prior to CSD for creosote oil and CO-24, as well as, those solvents of intermediate hydrogenation between them. Removal of the saturates of CO-48, the over-hydrogenated oil, could be more critical when applying the CSD method.

Cronauer et. al., (15) have noted that the saturates are usually less than 5 wt % of a typical coal liquefaction solvent. If 5% saturates in the form of decalin are assumed for a coal process solvent, then the data of Table 2 indicates the contribution of the saturates to the normalized H_2 volume would be 7.50 ml. This is only 5.68% of the normalized H_2 volume observed for CO-24. For a less hydrogenated oil such as CO-3, the contribution of the saturates under these assumptions would be 15.3%.

For creosote oil, the saturates separated by HPLC were 1.7 ± 0.1 wt % of the whole oil and for CO-24, 3.7 ± 0.6 %. These facts coupled with the relatively low H_2 yields observed for saturated model compounds

Table 9. Catalytic Solvent Dehydrogenation of Aromatic Fraction of Creosote Oils

Solvent	Mass, g	H ₂ , ml @ STP	Normalized H ₂ *, ml @ STP	Ave. Norm. H ₂ , ml @ STP
Creosote Oil	1.0000	25.0	25.0	24.4 ± 0.5
	0.9955	23.5	23.6	
	0.9987	24.6	24.6	
Creosote Oil, Arom. Frac.	1.0027	29.9	29.8	29.8
CO-24	0.0996	125	125	132 ± 7
	1.0033	139	139	
CO-24, Arom. Frac.	1.0010	136	136	136

* Normalized to one gram of reactant.

by CSD may obviate the need to remove saturates prior to CSD analysis for some solvents.

Conclusions

As the degree of hydrogenation of a creosote oil increased, its coal dissolution ability for W. Ky. 9/14 coal increased to an optimum and then declined beyond the optimum. The normalized H_2 volume obtained by CSD increased regularly as the degree of hydrogenation increased for the series of creosote oils up to the optimum level of coal dissolution. Beyond the optimum, the normalized H_2 volume increased only marginally as the level of solvent hydrogenation increased. The results suggest a gradual increase in the proportion of hydroaromatics contained in a hydrogenated creosote oil up to the level of optimum coal dissolution. Hydrogenation beyond the optimum level possibly caused a sharp increase in the proportion of saturates, which are known to be poor coal dissolution agents.

The light recycle oils and Mobil synthetic solvent were not as effective coal dissolution vehicles as hydrogenated creosote oils for a given normalized H_2 volume.

Nitrogen heterocyclic compounds did not appear to limit dehydrogenation reactions in the presence of $Pd/CaCO_3$. For the experimental conditions used, dehydrogenation of the coal solvents did not appear to be significantly limited by the buildup of H_2 partial pressure during the reaction.

Values of transferable hydrogen determined by catalytic dehydrogenation for three light recycle oils were in the same range as those determined by ^{13}C -NMR for other coal process solvents.

Application of catalytic dehydrogenation to aromatic fractions obtained by HPLC of creosote oil and the hydrogenated creosote oil, CO-24, gave normalized H_2 volumes similar to those of the whole oils. Removal of saturates prior to CSD analysis of some coal solvents may not be necessary.

V. APPLICATION OF ^{13}C -NMR to HYDROGENATED CREOSOTE OILS AND LIGHT RECYCLE OILS

Introduction

As described in the Introduction, Chap. II, ^{13}C -NMR analysis is probably the most important established method for the determination of hydroaromatic content of a coal liquefaction solvent (11).

Model compound evidence (31,32) indicates that the ^{13}C resonance of most carbon nuclei attached to hydroaromatic protons lie in the range of 22 to 31 ppm relative to tetramethylsilane (TMS). Aromatic ^{13}C resonances are generally between 100 to 160 ppm, and ^{13}C nuclei at saturated positions are in the range of 10 to 50 ppm.

The original work by Seshadri et al., on the measurement of hydroaromaticity by the ^{13}C method involved pretreatment by column chromatography to remove saturated hydrocarbons before ^{13}C analysis. As described in the Results and Discussion of Chap. IV, the saturates are typically less than 5 wt % of a liquefaction solvent. A simple calculation can indicate whether it is necessary to remove the saturates prior to ^{13}C analysis. Assume that the saturates of a typical coal solvent are an equal mixture of cis- and trans-decalin; also assume the solvent to be 90 wt % carbon. Then using the literature values for the ^{13}C chemical shifts of cis- and trans-decalin (13), it can be shown that the saturates would cause an overestimation of transferable H of 0.045 wt % for every 1.0 wt % saturates present. The solvent CO-24 was

was found by HPLC to contain 3.7 ± 0.6 wt % saturates; its transferable H by CSD was 1.34 ± 0.13 wt %. On the basis of such data, failure to remove the saturates of CO-24 would overestimate the transferable H using C^{13} -NMR by 14%.

CSD was generally applied to the whole oils in Chapter IV. For creosote oil and CO-24, dehydrogenation of aromatic/hydroaromatic fractions (minus saturates and polars) gave similar values of normalized H_2 volumes as the whole oils (Table 9).

This chapter describes the application of ^{13}C -NMR to selected hydrogenated creosote oils and light recycle oils previously analyzed by CSD. ^{13}C spectra are obtained on the whole oils. The best comparison of the CSD and ^{13}C methods would involve analysis of aromatic/hydroaromatic fractions for a series of solvents by the two methods. Positive errors in the determination of transferable H by either method are caused by the presence of saturates. It is, however, of interest to compare the results of CSD and ^{13}C -NMR analyses on the whole oils.

Experimental

Equipment

A Varian CFT-20 was used to obtain ^{13}C -NMR spectra. Instrumental conditions were identical to those chosen by Seshadri et al., (11). A pulse width of 7 μs was used; the tip angle equaled 42° ; the acquisition time was 1.024 s and the interval between pulses was 10 s. Approximately 2200 pulses were accumulated. Proton decoupling was on during data acquisition and between pulses. The sample tubes were 10 mm O.D. and obtained from Wilmad.

Materials

The hydrogenated creosote oils, light recycle oils and Mobil synthetic solvent are described in Chap. III. Samples were prepared by dissolving 1.5 g of oil in 2.4 g of deuteriochloroform (Aldrich, +99%). CDCl_3 served as both the locking solvent and the internal reference. Approximately six drops of TMS (Aldrich, +99%) were also added as a secondary reference.

Results and Discussion

The fraction of carbon atoms attached to hydroaromatic hydrogens, C_{HA} , is estimated from the integrated ^{13}C spectrum. Let

A = integrated spectral intensity from 100 to 160 ppm

S = integrated spectral intensity from 10 to 50 ppm

HA = integrated spectral intensity from 22 to 31 ppm

The quantity C_{HA} is defined as

$$C_{\text{HA}} = \frac{\text{HA}}{A + S}$$

The transferable H, the weight percent of hydroaromatic hydrogen, is

$$\text{Transferable H, wt \%} = \frac{C_{\text{HA}} (\text{wt \% of C})(1.0079)}{12.011}$$

Another useful parameter is the fraction of aromatic carbons, C_{A} .

$$C_{\text{A}} = \frac{A}{A + S}$$

The assignment of hydroaromatic carbon resonances to a fixed window such as 22 to 31 ppm ignores the fact that solvent shifts of

the order of 0.1 to 0.3 ppm can move some compounds into or out of the hydroaromatic region as different solvents are examined (13). It is, however, encouraging that the chemical shift of deuteriochloroform relative to TMS was a constant 77.1 ppm for all solvents examined.

Because of possible solvent shifts, ^{13}C chemical shift data quoted from the literature should be regarded as only approximate in this work to within 0.1 to 0.3 ppm. No attempt has been made to measure chemical shifts of model compounds in this work.

Additional problems concerning the ^{13}C method of measuring hydroaromaticity relate to possible hydroaromatics that lie outside the 22 to 31 ppm range or possible alkyl-substituted aromatics that may fall inside the range. For example, the CH_2 resonance of 9,10-dihydroanthracene is at 36.2 ppm (32); the methyl carbons of 1,8-dimethylnaphthalene resonate at 26.0 ppm (13).

Spectral intensity quantities A, S and HA plus the fractions C_A and C_{HA} are shown in Table 10. Experimental values of transferable H obtained by CSD and ^{13}C -NMR are compared in Table 11. The ^{13}C spectra of the selected solvents are shown in Appendix F.

Seshadri et al., (11) recommend that HA be corrected for the intensity of any acenaphthene (ACN) present. The methylene carbon resonance of ACN is 30.4 ppm relative to TMS (13). The correction is made by using the aromatic, β carbon signal of ACN at 119.0 ppm.

Seshadri and his coworkers argue that ACN should not be included among the sources of transferable H since they do not regard it as an effective hydrogen donor under coal liquefaction conditions. However, recent work in this laboratory (30) suggests that ACN may be a moderate

Table 10. Aromatic and Hydroaromatic Carbon Fractions in Hydrogenated Creosote Oils and Light Recycle Oils

Solvent	¹³ C-NMR Peak Areas, arbitrary units				C _A	C _S	C _{HA}	C _{HA} , ACN corr.
	A	S	HA	HA-ACN				
Creosote Oil	11.2	1.10	0.41	0.21	0.911	0.0894	0.033	0.017
CO-3	11.75	2.62	1.38	1.09	0.818	0.182	0.0960	0.0759
CO-24	9.00	5.85	3.66	3.51	0.606	0.394	0.246	0.236
CO-48*	3.09	6.69	3.60	3.60	0.316	0.684	0.368	0.368
CO-48**	4.57	10.67	5.59	5.59	0.300	0.700	0.367	0.367
LR0-1	7.69	4.48	2.00	1.54	0.632	0.368	0.167	0.127
LR0-3	6.28	6.39	2.57	2.40	0.496	0.504	0.203	0.189
Mobil Synthetic	10.06	4.10	2.78		0.710		0.196	

* 2211 pulses accumulated.

** 3170 pulses accumulated.

Table 11. Transferable H of Solvents by CSD and ^{13}C -NMR

Solvent	Transferable H, wt %		
	CSD	^{13}C -NMR	^{13}C -NMR, ACN corr.
Creosote Oil	0.219 ± 0.005	0.25	0.13*
C0-3	0.441 ± 0.006	0.730	0.577
C0-24	1.34 ± 0.13	1.84	1.77
C0-48	1.40 ± 0.09	2.75 ± 0.01	2.75 ± 0.01
LR0-1	0.480 ± 0.007	1.20	0.931
LR0-3	0.602 ± 0.047	1.47	1.37
Mobil Synthetic**	1.19 ± 0.03	1.47	

*The intensity of HA could only be measured to two significant figures for creosote oil. All other intensities were measured to three significant figures.

**Actual value is 1.26 wt %.

hydrogen donor in coal liquefaction. Coal dissolution experiments were run in solutions of 1-methylnaphthalene plus a fixed number of moles of selected hydrogen donors. The coal was W. Ky. 9/14. The coal conversions by THF solubles for 1-methylnaphthalene, indan, acenaphthene and tetralin were respectively: 18.6, 26.9, 29.9 and 43.6 wt %.

The ability of acenaphthene/1-methylnaphthalene to evolve H_2 under CSD conditions has already been noted (Chap. II). However, it was not possible to define the stoichiometry of the dehydrogenation process. Given the fact that ACN could be contributing to the volume of H_2 collected in the CSD of the various coal-derived solvents, it was decided to calculate the transferable H by ^{13}C -NMR both including and excluding ACN.

Correcting for the presence of ACN lowers the value of transferable H. The correction is greatest for solvents such as creosote oil that contain a small quantity of saturates.

The reproducibility of the ^{13}C technique was checked by obtaining spectra on two different samples of CO-48. The first spectrum was from the accumulation of 2211 pulses and the second spectrum the sum of 3170 pulses. The values of C_A were 0.316 and 0.300, respectively; the values of C_{HA} were 0.368 and 0.367. For this particular solvent, the reproducibility appears adequate.

The Mobil synthetic solvent can be used to test the accuracy of the ^{13}C method using the experimental parameters suggested by Seshadri. CSD has already been applied to the solvent. The actual values of C_A and C_{HA} are 0.771 and 0.169, respectively. The corresponding

experimental values determined by the Seshadri ^{13}C method were 0.710 and 0.196. It is not possible to estimate C_A by CSD, but the experimental value of C_{HA} by CSD was 0.159 ± 0.004 .

For the Mobil solvent, the ^{13}C method of Seshadri overestimates C_{HA} , the fraction of hydroaromatic carbons, by 16%. The ^{13}C method underestimates C_A , the fraction of aromatic carbons, by 7.9%. Seshadri et al., observed a similar result for a mixture of 9,10-dihydrophenanthrene, octahydrophenanthrene and tetrahydropyrene. For their mixture, ^{13}C overestimated C_{HA} by 8.8%.

Nuclear magnetic resonance experiments are very susceptible to a power-saturation phenomenon (33). A spectral line in NMR is seen as a result of a decrease in the level of incident rf power during resonance. The intensity, I , of a NMR signal is directly proportional to the rf power, E , and the population difference between the lower and upper nuclear energy levels, $n_- - n_+$.

$$I \propto E(n_- - n_+)$$

Because nuclear spin energies are quite small compared to usual thermal energies, only a very small population difference can be established in a typical NMR experiment.

To obtain a maximum signal intensity, one should obviously operate at a high level of rf power. However, during resonance, when the energy of the rf field is adjusted to equal the energy difference of the spin states established by the external magnetic field, the population of the two spin states tend to equalize. When the population difference decreases, the extent of absorption of rf power decreases. To tune

a continuous rf magnetic resonance spectrometer, one typically raises the rf power from some level low enough that I can be observed to increase concomitantly. As E increases, a point is reached where a significant equalization of the spin populations occurs. At this point the intensity of a spectral line begins to decrease, and the line is said to saturate.

Pulsed spectrometers use short time bursts of high level rf power to excite all the nuclei of a sample simultaneously. Not only is the level of rf power (tip angle) important with pulsed spectrometers, but also the time delay between pulses.

Saturation is limited by the tendency of the spin-lattice relaxation process to return nuclei from the upper energy state to the lower state. The relaxation process is characterized by a spin-lattice relaxation time, T_1 . The spin-lattice relaxation time is the time needed for a spin population difference at resonance to increase to 63% of the equilibrium population difference (no resonance).

In pulsed NMR experiments, there must be sufficient time between rf pulses for the spin-lattice process to return excited nuclei to the lower energy level if saturation is to be avoided. Generally, T_1 values vary for different carbon nuclei in a molecule. The interval between pulses should be several times the largest T_1 value of the sample.

The main deficiency of ^{13}C -NMR when determining carbon distributions is the nuclear Overhauser enhancement (NOE) that occurs for protonated carbons versus nonprotonated (quaternary) carbons. Non-protonated carbon nuclei have considerably longer spin-lattice

relaxation times than the secondary or tertiary carbons of a typical hydroaromatic molecule. The result is that the NMR signal of quaternary carbons tend to saturate more readily than the other carbon signals. The relative oversaturation of the quaternary carbon signals reduces the intensity of those spectral lines compared to the lines of the protonated carbons.

The instrumental conditions recommended by Seshadri for data acquisition attempt to minimize the NOE effect by decoupling the proton spins from the carbon nuclei both during signal accumulation (1.024 s) and between pulses (10 s). The interval between pulses is quite long compared to normal conditions where NOE is not a consideration. A longer interval between pulses allows more time for the ^{13}C nuclei to return to the steady-state value of z-magnetization (less saturation); however, increasing the interval between pulses lengthens the time needed to accumulate a sufficient number of pulses for an adequate signal-to-noise ratio. At least seven hours were required to accumulate the data for a single spectrum in this work. Also, the Seshadri method uses a low tip angle (42°) to help reduce the saturation effect. 90° is a usual tip angle where the determination of relative spectral intensities are not critical.

The overestimation of C_{HA} and underestimation of C_{A} for the Mobil solvent are probably due to a residual NOE effect. The only peaks observed in the 22 to 31 ppm range of the Mobil solvent spectrum are those of the tetralin α hydroaromatic carbons (29.3 ppm) and β hydroaromatic carbons (23.2 ppm). Too large a value of C_{HA} cannot be ascribed to interfering saturates. The two spectral lines of the

hydroaromatic carbons of tetralin should be equal in intensity. It was observed (Figure 24) that the peak height of the α line was approximately 10% greater than that of the β line.

The value of C_{HA} determined by CSD for the Mobil solvent was smaller than the correct value by 5.9% (versus 16% overestimation for ^{13}C -NMR). This underestimation probably reflects a lack of sufficient reaction time for the establishment of equilibrium in the dehydrogenation of tetralin. Dehydrogenation of tetralin in the presence of 1-methylnaphthalene gave a hydrogen yield of $89.9 \pm 3.9\%$ (Table 2) under the CSD conditions. Thermodynamic calculations (Appendix C) predicted a 99.17% H_2 yield.

For the Mobil solvent, the expected value of transferable H was 1.26 wt %. The values by CSD and ^{13}C -NMR were 1.19 ± 0.03 and 1.47 wt %, respectively.

For all the solvents examined, the value of transferable H as determined by ^{13}C -NMR (corrected or uncorrected for acenaphthene) was larger than the CSD value with one exception. The exception was the acenaphthene-corrected value for creosote oil.

As shown in Figure 10, there is a smooth relationship between the measurements of transferable H by CSD or ^{13}C -NMR for all the solvents examined. The ^{13}C data uncorrected for acenaphthene is used in Figure 10. The results suggest qualitatively that the two methods are measuring some of the same quantities.

Because of the NOE effect it is expected that the ^{13}C -NMR method will tend to overestimate transferable H. The presence of saturates and sidechains on aromatic rings may also cause the value of

Figure 10. Transferable H by CSD and ^{13}C -NMR (uncorrected)

transferable H to seem too large when estimated by the ^{13}C method for whole oils. Saturates such as decalin do resonate in the 22 to 31 ppm range. For example, the α carbon resonance of cis-decalin is 30.2 ppm, and the β carbon resonance is 24.2 ppm (13).

From the HPLC fractionation work, the saturates were estimated to be 1.7 ± 0.1 wt % of the creosote oil and 3.7 ± 0.6 wt % of CO-24. It is instructive to assume that the saturates are decalin and estimate a "saturates-corrected transferable H" for the two solvents. For CSD, the correction factor is 0.013 wt % transferable H for every 1.0 wt % saturates. This value is based upon the CSD results of decalin (Table 2). For ^{13}C -NMR, the factor is 0.045 wt % transferable H for every 1.0 wt % saturates. The calculation results are shown in Table 12.

Among the creosote oils, it is expected that the largest correction for saturates would be applied to CO-48. The fraction of saturated carbons, C_S , provides a measure of the degree of saturation.

$$C_S = \frac{S}{A + S} = 1 - C_A$$

It should be noted that C_S includes the hydroaromatic carbon. The values of C_S (Table 10) for LRO-1 and LRO-3 are 0.368 and 0.504, respectively. For CO-24 and CO-48, the values of C_S are 0.394 and 0.692 ± 0.008 , respectively. Using the assumption of saturates as decalin, the transferable H of CO-24 was corrected from 1.84 to 1.67. Comparable or larger corrections may be expected for the transferable H of CO-48, LRO-1 and LRO-3.

Table 12. Saturates-Corrected Transferable H

Solvent	Transferable H, wt %	
	CSD	¹³ C-NMR
Creosote Oil	0.219 ± 0.005	0.25
Creosote Oil, Saturates Corrected	0.197	0.17
CO-24	1.34 ± 0.13	1.84
CO-24, Saturates Corrected	1.29	1.67

Plots of coal dissolution yield versus aromatic carbon fraction, transferable H by ^{13}C -NMR uncorrected for acenaphthene, transferable H by ^{13}C -NMR corrected for acenaphthene and transferable H by CSD are presented in Figures 11-14. In all cases, the results are similar to those found by Jeng (3,17). A smooth correlation exists for the creosote oils, but the light recycle oils cannot be fitted to the curve defined by the creosote oils.

Conclusions

Values of transferable H measured by ^{13}C -NMR, whether corrected or uncorrected for acenaphthene, were generally larger than the corresponding values obtained by CSD.

The ^{13}C -NMR method overestimated the transferable H of the Mobil solvent by 16.7%. The overestimation was probably due to a residual NOE effect. CSD of the Mobil solvent gave a value of transferable H within 5.6% of the correct value.

Smooth correlations were found between coal conversion and transferable H as determined by ^{13}C -NMR. The light recycle oils could not be fitted to the curve defined by the creosote oils. The correlations were similar to that based on CSD data.

Recommendations

The CSD experiments on model compounds were generally encouraging. The method did dehydrogenate a number of hydroaromatic compounds containing six-member rings to the extent of 90% or better. Alkyl side-chains and saturated compounds dehydrogenated less extensively.

Figure 11. Coal Dissolution Yield vs. Aromatic Carbon Fraction

Figure 12. Coal Dissolution Yield vs. Transferable H by ^{13}C -NMR, Uncorrected for Acenaphthene

Figure 13. Coal Dissolution Yield vs. Transferable H by ^{13}C -NMR, Corrected for Acenaphthere

Figure 14. Coal Dissolution Yield vs. Transferable H by CSD

It was not possible, however, to determine the source of H_2 evolution when CSD was applied to acenaphthene. Further work is needed to define the stoichiometry of the acenaphthene dehydrogenation reaction. Material losses were found in the CSD of acenaphthene. The losses were probably the result of coking or condensation reactions. It has been reported that acenaphthylene thermally polymerizes at $130^\circ C$ (34). It would be of interest to identify the products of acenaphthene dehydrogenation by HPLC or thin-layer chromatography (TLC).

The products of model compound dehydrogenations were generally verified to be as expected by GC analysis. An interesting experiment would be to compare the ^{13}C -NMR spectrum of a hydrogenated creosote oil or LRO to the spectrum of the product of that same oil after CSD. The fraction of aromatic carbons, C_A , should increase after dehydrogenation, and the fraction of hydroaromatic carbons, C_{HA} , should decrease. It might be possible to better define the sources of hydrogen evolution for CSD of the coal-process solvents by such an experiment.

More work on the ^{13}C -NMR method of determining hydroaromaticity is needed. Additional model compound mixtures should be investigated to verify that the over-estimation of C_{HA} by ^{13}C -NMR is a result of NOE. A careful study of instrumental parameters and/or the use of paramagnetic relaxation agents such as chromium acetylacetonate to minimize the NOE effect would be useful (11). The extent of possible solvent shifts in ^{13}C spectral lines can be investigated by spiking some typical coal solvents with model compounds. The methyl ^{13}C resonance of 3-methylphenanthrene at 22.05 ppm (32) might provide a good test case for the possible shift of ^{13}C resonances near the 22 to 31 ppm window.

The calculations on transferable H corrected for saturates (Table 12) suggest that ^{13}C -NMR may be more sensitive to the presence of saturates than CSD. The two methods, CSD and ^{13}C -NMR, need to be compared using aromatic/hydroaromatic fractions of the whole oils. The fractions would be prepared by HPLC (25). The solvent C0-48 should provide an excellent test since it was determined to have the largest fraction of saturates (Table 10).

The inability to fit the light recycle oils to any of the various correlations applied to the hydrogenated creosote oils concerning coal conversion is a very fundamental problem. It implies that other parameters than the hydroaromatic hydrogen content of the solvent are important to the mechanism of coal dissolution. Other parameters of relevance may include solvent viscosity, chemical functionality, the presence of five-member ring compounds and solvent polarity.

It would be of interest to determine if there is any detectable difference in the dielectric constants for the solvents used in this work. Solvent polarity is readily related to dielectric constant.

Also, variations in the quantity of heteroatoms are clues to changes in solvent polarity and functionality. The 16.2% drop in the coal dissolution yield of C0-24 compared to C0-48 has been discussed previously in terms of an increase in the proportion of saturates (Table 5). It is interesting to note (Table 4) that for all the hydrogenated creosote oils except C0-48 there is a small quantity of nitrogen present (0.44 to 1.18 wt %). The nitrogen content of C0-48 is experimentally undetectable.

It might be useful to run coal dissolution experiments on the CO-48 solvent to which enough quinoline was added to bring the overall nitrogen content to about 0.5 wt %. It is well known that 1,2,3,4-tetrahydroquinoline (THQ) is an excellent coal dissolution solvent. A small quantity of THQ might function as a better hydrogen-shuttling agent than typical hydroaromatics such as tetralin. THQ could be formed from quinoline by hydrogen exchange with hydroaromatics in the solvent. Neat tetralin was also found to be a poorer coal dissolution solvent than CO-24 (Fig. 6). A similar experiment involving the doping of tetralin with quinoline might be of interest.

VI. THE USE OF CYCLOHEXENE AS A SCREENING AGENT FOR WEAKLY CATALYTIC MATERIALS IN COAL SOLVOLYSIS

Introduction

To supply the industrialized world with sufficient hydrocarbon fuels and chemical feedstocks over the long term, abundant hydrocarbon sources such as coal, shale oil, and tar sands must ultimately be utilized. Direct non-catalytic liquefaction of coal provides a liquefied product with a somewhat increased hydrocarbon content. To increase the hydrogen content of the liquefied product to the level necessary for transportation fuels or for chemical feedstocks, catalysts which promote hydrogenation or hydrocracking must be employed. Minerals indigenous to coal provide an internal and inexpensive source of catalytic activity. Another readily accessible and inexpensive source of catalytic minerals is the use of oxidized coal liquefaction residues or pyritic residues resulting from coal cleaning.

Previous work has shown that clay minerals (35-38) and pyrite (39-42) aid in coal dissolution and promote hydrogen transfer reactions. Liquefaction residues that have been oxidized have been shown to increase the pentane soluble yield of liquefied coal (43). Although a considerable amount of empirical evidence has been amassed which shows that clay minerals, pyrite and liquefaction residues do possess catalytic activity during coal liquefaction, little is known about how these minerals function as catalysts or their relative selectivity for

various reactions such as hydrogenation, isomerization or hydrocracking. This work is an investigative study using a sensitive probe reaction, cyclohexene reacted in the presence of mineral and oxide additives at liquefaction conditions.

Experimental

Materials

Cyclohexene (+99% purity) was obtained from Aldrich and was used as received. Octane (+99% purity) obtained from Aldrich was dried over molecular sieves before use. Kaolinite, $(\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4)$, 13 m²/g, from Burgess Pigment Co., montmorillonite $((\text{Na,Ca})_{0.33}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}\text{OH}\cdot n\text{H}_2\text{O})$, 17 m²/g, from Georgia Kaolin Co., illite $(\text{K}(\text{Al,Si})_3\text{O}_{10}(\text{OH})_2)$, from Source Clay Mineral Repository, University of Missouri, ilmenite (FeTiO_3) from Pesses Co., dolomite $(\text{CaMg}(\text{CO}_3)_2)$ from David New Minerals, aluminum oxide (C) (Al_2O_3) , 100 m²/g, from Degussa, silica (SiO_2) , 50 m²/g, from Degussa, titanium oxide (P-25) (TiO_2) , 50 m²/g, from Degussa were washed in acetone and air-dried. Pyrite (FeS_2) obtained from Juan Montál in Vilafranca, Spain was ground to -200 mesh. Kerr McGee residue was obtained from the Wilsonville Advanced Coal Research and Development Facility at Wilsonville, Alabama. Two grams of the liquefaction residue was ashed for three hours at 700°C under an air flow of 150 ml/min.

Reaction Procedure

Cyclohexene reactions were performed in a 15 cm³ stainless steel microreactor equipped at one end with a Nupro fine metering valve for pressurizing with hydrogen. For these reactions, one gram of

cyclohexene was diluted in three grams of octane in the reactor which was pressurized to 900 psig at 25°C. One gram of mineral catalyst was added to the reaction mixture. The microreactor was then heated to 400°C for 60 minutes and agitated at 800 RPM. After reaction, the reactor was immediately quenched in cold water.

A weighed aliquot of the reaction products were analyzed by gas chromatography using an Apiezon L glass capillary column and FID detection. The column was temperature programmed from 60°C to 220°C at a program rate of 15°C/min. Initial and final temperatures were held for twenty-five and thirty minutes, respectively. n-Heptane was used as an internal standard.

Vacuum Fractionation of Reaction Products

One gram of cyclohexene diluted in three grams of octane pressurized with 900 psig of H₂ at room temperature was reacted in the presence of one gram of kaolinite for one hour at 400°C. The reaction products were fractionated under vacuum at 26°C. After four hours 3.38 g of materials had been collected. The temperature was then raised to 225°C. After four more hours, an additional 0.36 g was collected. Both fractions were analyzed by gas chromatography using an Apiezon L glass SCOT column with FID detection, and temperature programming from 50°C to 185°C at 25°C/min with holds at initial and final times of 15 and 20 minutes, respectively. Ethylbenzene was used as an internal standard.

The product gases were analyzed by gas chromatography. An 8 ft Porapak Q followed by an 8 ft Porapak R column was programmed from 40°C to 225°C at 20°C/min. Thermal conductivity detection was used.

X-ray Analysis

Several minerals and the liquefaction residue were analyzed by x-ray diffraction using a Norelco diffractometer. The analysis of kaolinite showed no major impurities. The diffractogram of the silica used showed a broad peak indicating an amorphous material. X-ray analysis of a liquefaction residue ash showed the major constituents to be hematite, aluminum oxide, silica, mica and smectite or chlorite.

Results

Cyclohexene readily undergoes hydrogenation, isomerization and cracking in the presence of catalysts at appropriate reaction conditions. The reaction sequence normally proposed is

The reaction in the presence of a hydrogenation catalyst gives cyclohexane (II) and methylcyclopentane (III) as reaction products. In the presence of acid catalysts the typical reaction products are the isomerized products, 1-methylcyclopentene (IV) and 3-methylcyclopentene (V).

The activity of clay minerals and pyrite minerals indigenous to coal, oxides typical of catalyst supports and liquefaction residue ashes were examined using the cyclohexene reaction. The product distribution resulting from each reaction is given in Table 13. For ease of comparison of the activity of the different additives, three parameters have been defined to describe the type and quantity of reaction occurring in the cyclohexene reaction mixture. These parameters are: (1) percent hydrogenation which is the mole percents of cyclohexane and methylcyclopentane; (2) percent isomerization, mole percent of methylcyclopentane, 1-methylcyclopentene plus 3-methylcyclopentene; and (3) percent recovery in weight percent. All three parameters are based on the cyclohexene charged. Appendix E details the calculation procedures.

A compilation of the activity of each catalyst in terms of the parameters given above are presented in Figures 15 and 16. The activity of the different types of additives vary considerably but can be grouped according to their compositional type. Reaction of cyclohexene in the absence of any additive showed 3.82% hydrogenation but no isomerization.

The clays, kaolinite, montmorillonite, and illite showed activity for both hydrogenation and isomerization with isomerization being the more predominant reaction. Of the three clays, kaolinite was the most active in both isomerization and hydrogenation. The activity levels of montmorillonite and illite were similar. Recovery of the reaction mixture was low in all three cases with kaolinite yielding ~40%, illite ~50% and montmorillonite ~60%. Since in all three cases the total

Table 13. Product Distribution of Cyclohexene Reaction

Additive	Product Distribution, mole %					Unrecovered, wt %
	cyclo- hexane	methyl- cyclo- pentane	1-methyl- cyclo- pentene	3-methyl- cyclo- pentene	cyclo- hexene	
Blank	3.1	0	0	0	97.0	0
Kaolinite	4.3 ± 0.36	6.7 ± 0.25	14.9 ± 0.11	3.7 ± 0.21	9.9 ± 0.89	60.2
Montmorillonite	4.2 ± 0.73	3.0 ± 0.60	8.9 ± 1.1	2.4 ± 0.26	42.0 ± 3.1	39.4
Illite	4.8 ± 0.28	3.0 ± 0.16	2.6 ± 0.18	10.3 ± 0.63	29.1 ± 1.2	50.3
Dolomite	7.3 ± 1.7	3.0	0.41 ± 0.18	0.11 ± 0.12	67.7 ± 5.0	24.3
Ilmenite	5.9 ± 1.4	0.25 ± 0.12	2.7 ± 1.0	1.1 ± 0.32	68.8 ± 7.2	21.2
Aluminum Oxide	3.2 ± 1.7	0.34 ± 0.26	8.3 ± 0.85	2.2 ± 0.07	66.4 ± 5.6	14.4
Titanium Oxide	10.5 ± 0.36	7.7 ± 0.61	17.5 ± 0.93	3.8 ± 0.9	11.7 ± 0.90	48.9
Iron Pyrite	13.7 ± 1.3	0.53 ± 0.16	0.55 ± 0.63	0.0	48.2 ± 5.0	31.5
Liquefaction Residue Ash	81.8 ± 4.8	1.4 ± 0.91	0.09 ± 0.10	0.0	0.48 ± 0.5	13.8

Figure 15. Catalysis of Cyclohexene Reactions by Clay Minerals and Naturally Occurring Oxides

Figure 16. Catalysis of Cyclohexene Reactions by Pyrite and Kerr McGee Ash

volume of liquid recovered was much less than the amount of liquid charged, it is postulated that a portion of the reactants are adsorbed on the catalyst surface. An analysis of the gas phase showed the gas to be 99% hydrogen.

To determine if the unrecovered material is adsorbed or coked on the catalyst surface, an octane/cyclohexene/kaolinite product mixture was vacuum distilled at 26°C. After four hours, 3.38 g of the initial 4.00 g charge was recovered. The temperature was then raised to 225°C and after another four hours an additional 0.36 g was collected. Each collected fraction was analyzed by gas chromatography using a SCOT Apiezon L glass capillary column. Comparison of the chromatograms given in Figure 17 shows the presence of high boiling constituents in both vacuum distilled products. A material balance based on the gas chromatographic analysis of the vacuum distilled fractions indicates (Table 14) that 2.99 g of octane was recovered from the combined fractions yielding 99.3 wt % of initial octane charge. The amount of cyclohexene recovered from the combined fractions was 0.051 g, i.e. 5.1 wt % of the cyclohexene charge. By difference, the cyclohexene reacted was 94.9 wt % with the identifiable C_6 compounds yielding 26.5 wt % and the observable high boiling compounds composing 44 wt % of the product. Even after vacuum fractionation at 225°C for four hours 24.4 wt % of the initial cyclohexene charged was not recovered.

Iron pyrite, a metal sulfide, promotes the hydrogenation (19.2%) of cyclohexene to cyclohexane. Only ~1.1% isomerization occurred and 68.5% of the reaction mixture was recovered. Dolomite, a carbonate of

Figure 17. Chromatograms of Vacuum-Fractionated Products of Cyclohexene/Octane Hydrogenation in the Presence of Kaolinite

Table 14. Product Distributions of Fractionated Products Using Kaolinite as an Additive

Components	Product Distribution of Reaction Products, g		
	Fraction 1	Fraction 2	Total Product
Cyclohexane	0.076	7.6×10^{-4}	0.077
Methylcyclopentane	0.070	9.7×10^{-4}	0.071
1-Methylcyclopentene	0.095	1.5×10^{-3}	0.096
3-Methylcyclopentene	0.021	3.1×10^{-4}	0.021
Cyclohexene	0.050	6.8×10^{-4}	0.051
Octane	2.90	0.088	2.99
High Molecular Weight	0.17	0.27	0.44
Total Recovery	3.38 ± 0.03	0.36 ± 0.02	3.74

calcium and magnesium, also promoted only hydrogenation, 7.3%, but less than that attributed to iron pyrite.

The oxide additives were all active in both hydrogenation and isomerization but to varying degrees. Ilmenite, a mixed iron titanium oxide showed the least activity. Titanium oxide was the most active of the oxides having a slightly greater activity for isomerization than kaolinite, 28.5% compared to 25.3%, and a slightly lower hydrogenation than pyrite, 17.7% versus 19.2%.

The liquefaction residue ash composed chiefly of silica, hematite, alumina, mica and smectite provided the greatest hydrogenation activity of any of the additives (83.6%). Minimal isomerization, 1.8%, was observed and 86% of the product was recovered.

In Table 15, the data resulting from cyclohexene/octane reactions occurring in the presence of silica shows a high degree of inconsistency in the results. Postulating that the differences were due to differing amounts of water contacting the silica during the reaction, the reaction mixture was doped with additional water. After reaction, the reaction product was solid and could not be recovered. X-ray diffraction analysis showed the silica to be an amorphous material, giving a very broad peak where crystalline silica normally gives a sharp peak.

Discussion

The minerals used in this work are likely to be present in coal liquefaction reactors and may serve as active surfaces for the promotion or inhibition of liquefaction reactions. The clays and pyrite are indigenous to most coals. The oxides used are typically used as

Table 15. Reactions Occurring in Cyclohexene System Using Silica as an Additive

	Hydrogenation, mole %	Isomerization, mole %	Recovery, wt %
Dried Silica	3.70 ± 0.42	31.59 ± 6.0	68.08
	2.40 ± 0.60	6.22 ± 0.55	92.12
	10.69 ± 1.70	27.40 ± 1.36	47.94
	12.49 ± 2.27	27.30 ± 1.32	46.22
	6.72 ± 1.16	6.30 ± 1.35	79.94
Silica with Water Addition			0

catalyst supports and are likely to be present in catalytic liquefaction. Some of the materials used in this study are readily available and are waste products from coal processing. Pyrite is available in a concentrate from coal beneficiation, and the liquefaction residues are produced during the separation step in coal processing.

Clays were used as the first cracking catalysts and have since been replaced by the more active and selective zeolites. Although not as active as the zeolites, the proximity of the clays finely distributed and embedded in the coal matrix make them highly accessible and important in catalyzing reactions occurring during the dissolution of coal. The mineralogically authentic clays obtained for this study are used with minimal pretreatment and should be representative of those present in coal. As stated in the Results, the activity of the alumina silicate clays in the cyclohexene reaction is primarily in hydrogenation and isomerization. Although the exact nature of reactions occurring during liquefaction depends upon the chemical composition of the coal/slurry mixture and the reaction conditions, the reactions of cyclohexene in the presence of these additives at liquefaction conditions may typify the reactions promoted by the clays during coal liquefaction.

A logical extension of this work is to consider the effects of the hydrogenating and isomerization ability of clays for a reactive intermediate such as dihydronaphthalene known to be present in coal liquids during liquefaction. By promoting hydrogenation, the clays may catalyze the formation of tetralin, a known hydrogen donor and an effective solvent for coal conversion. In contrast, by promoting isomerization, the dihydronaphthalene would isomerize to form 1-methylindene or

1-methylindan both of which are poor hydrogen donors and ineffective solvents for coal. Further work is necessary to substantiate this hypothesis.

The formation of high boiling adducts resulting from cyclohexene reaction in the presence of kaolinite (Table 14) is indicative of the formation of coke precursors on the catalyst surface. The rate of coking on the catalyst surface has been shown to increase with the acidity of the catalyst and the proximity of the acid sites on the catalyst surface. In addition, coke formation requires a source of hydrogen which is generated by a coke precursor and a sink for hydrogen such as an olefin (44). The production of these high molecular weight species in a simple system such as cyclohexene indicates that acidic clays may promote retrogressive reactions in the complex coal liquids during liquefaction resulting in the formation of high molecular weight and difficult to dissolve materials. This coke formation is detrimental to the overall conversion of the coal liquefaction process.

Pyrite is a prevalent mineral component in most coals and is normally finely dispersed throughout the coal. This work shows pyrite to be a mild hydrogenation catalyst for cyclohexene. It is likely that increased surface area such as that of dispersed pyrite in coal may be more effective in hydrogenation than the ground <200 mesh mineralogical pyrite. The lack of isomerization and the substantial recovery of the cyclohexene indicates that the pyrite contains essentially no surface acid sites.

Ilmenite, (FeTiO_3), and dolomite ($\text{CaMg}(\text{CO}_3)_2$) used as additives under the same conditions as the clays show a much lower ability to

isomerize cyclohexene, indicating a lower surface acidity. Ilmenite and dolomite have similar hydrogenation activity as the clays but do not have the activity of pyrite. Recovery from these additives is much higher than from the clays, which supports the premise of their having lower surface acidity which results in less coke formation. Neither dolomite nor ilmenite appear to be detrimental to liquefaction and if present may promote some of the reactions involved in liquefaction.

Both aluminum oxide and titanium oxide show activity for the isomerization and hydrogenation of cyclohexene, with titanium oxide being nearly equivalent to pyrite in hydrogenation and more active than kaolinite for isomerization. Only one half of the cyclohexene reaction products can be recovered from the reaction mixture when TiO_2 is used as the additive. Both the high degree of isomerization and the apparent coking of the cyclohexene by TiO_2 indicate a high surface acidity. Aluminum oxide is not by itself considered to be an active cracking catalyst and has a low surface acidity. The experimental results bear this out with aluminum oxide promoting 10.8% isomerization of cyclohexene and allowing a recovery of greater than 85%.

Oxidized liquefaction residue gives the greatest activity of any of the additives used. The residue ash hydrogenates ~82% of the cyclohexene and shows no activity for isomerization. The lack of isomerization activity and the high recovery of the cyclohexene product suggests a nonacidic surface. The chief components of the residue ash are silica, alumina, hematite and two silica-alumina clays. Compositionally, all of these components are active individually and seem to have

a synergetic effect when reacted together. In the reductive atmosphere of these experiments, the hematite reduces to metallic iron which has been shown to be a hydrogenation catalyst (23). The activity of the oxidized liquefaction residue is very sensitive to the method of production; the factors which affect its effectiveness include the length of time and temperature of heating, the air flow, and residue loading. This sensitivity may result from particle size effects, surface acidity, or trace metal composition. Further work is needed in this area to optimize the composition of the ash.

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APPENDICES

APPENDIX A
STRUCTURAL FORMULAS AND NAMES OF MODEL COMPOUNDS
AND EXPECTED DEHYDROGENATION PRODUCTS

Table 16. Structural Formulas and Names of Model Compounds and Expected Dehydrogenation Products

Compound	Dehydrogenation Product

1,2-Dihydronaphthalene	Naphthalene

1,4-Dihydronaphthalene	Naphthalene

Tetralin	Naphthalene

9,10-Dihydrophenanthrene	Phenanthrene

Table 16, continued

Compound	Dehydrogenation Product
9,10-Dihydroanthracene	Anthracene
1,2,3,4,5,6,7,8-Octahydroanthracene	Anthracene
1,2,2a,3,4,5-Hexahdropyrene	Pyrene
1-n-Decyl- 3,4,5,8,9,10-Hexahdropyrene	Various Sidechain Dehydrogenation Products

Table 16, continued

Compound	Dehydrogenation Product

Acenaphthene	Acenaphthylene

1,2,3,4-Tetrahydroquinoline	Quinoline

Ethylbenzene	Styrene

Indan	Indene

Decalin	Naphthalene

Table 16, continued

Compound	Dehydrogenation Product
$\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$	C_{16}H_n
Hexadecane	Various Dehydrogenation Products
None
Fluorene
None
O-Cresol
None
β-Naphthol	

APPENDIX B

GAS. CHROMATOGRAPHY CONDITIONS

Chromatographic analysis of the model compounds and the products of CSD were performed on a Varian Model 3700 Chromatograph with FI detection. A glass capillary or a packed (SP-2250) column was used for the various analyses (see Chap. II, Experimental).

For all injections, the column was kept isothermal. The injector temperature of the capillary column was always 220°C; the detector temperature was 240°C. The injector temperature of the SP-2250 column was always 10°C above the column temperature; the detector temperature was kept at 360°C for all runs. Table 17 gives the column temperature and the column used for the various model compounds.

Table 17. Column Temperatures for Model Compound Dehydrogenation Products

Compound	GC Column*	Temp., °C
1,2-Dihydronaphthalene	Cap	200
1,4-Dihydronaphthalene	Cap	200
Tetralin	Cap	200
9,10-Dihydrophenanthrene	SP-2250	170
9,10-Dihydroanthracene	SP-2250	170
1,2,3,4,5,6,7,8-Octahydroanthracene	SP-2250	170
1,2,2a,3,4,5-Hexahdropyrene	SP-2250	240
1-n-Decyl- 3,4,5,8,9,10-Hexahdropyrene	SP-2250	260
Acenaphthene	Cap	210
1,2,3,4-Tetrahydroquinoline	SP-2250	130
Ethylbenzene	Cap	150
Indan	Cap	210
Decalin	Cap	180
Hexadecane	SP-2250	200
Fluorene	SP-2250	170
o-Cresol	SP-2250	180
β-Naphthol	SP-2250	180

* The capillary column is designated as Cap.

APPENDIX C
THERMODYNAMIC CALCULATIONS FOR
TETRALIN EQUILIBRIUM CONVERSION

The dehydrogenation equilibrium of tetralin to naphthalene has been studied by Wilson et. al, (22) in the gas phase. The reaction is

Using the designation T for tetralin and N for naphthalene, the equilibrium equation can be written as

$$K_p = \frac{p_N p_{H_2}^2}{p_T} \quad (1)$$

where K_p = equilibrium constant, and p_{H_2} = partial pressure of H_2 , etc. In terms of the total pressure, P , and the component mole fractions, y_i

$$\begin{aligned} p_T &= y_T P \\ p_N &= y_N P \\ p_{H_2} &= y_{H_2} P \end{aligned} \quad (2)$$

Let n_T = moles of tetralin initially charged and θ = degree of tetralin dehydrogenation at equilibrium, then

$$\text{moles of T at equil.} = n_T (1-\theta)$$

$$\text{moles of N at equil.} = n_T \theta$$

$$\text{moles of } H_2 \text{ at equil.} = 2n_T \theta$$

$$\text{Total moles at equil.} = n_T (1+2\theta) + n_I = n$$

The above equations assume that only tetralin and some inert material, n_I , are present initially.

Eqs. (2) can then be written

$$p_T = \frac{n_T (1-\theta) P}{n_T (1+2\theta) + n_I}$$

$$p_N = \frac{n_T \theta P}{n_T (1+2\theta) + n_I}$$

$$p_{H_2} = \frac{2n_T \theta P}{n_T (1+2\theta) + n_I}$$

Substituting the partial pressure expressions into Eq. (1)

$$K_p = \frac{4\theta^3 n_T^2 P^2}{(1-\theta)[n_T (1+2\theta) + n_I]^2}$$

Defining $r = n_I/n_T$,

$$K_p = \frac{4\theta^3 P^2}{(1-\theta)(1+2\theta+r)^2} \quad (3)$$

Using the ideal gas law, the pressure can be expressed as

$$P = n_T (1+2\theta+r) \frac{RT}{V} \quad (4)$$

where T = temperature, V = volume, and R = ideal gas constant. Substituting Eq. (4) in (3),

$$K_p = \frac{4\theta^3 n_T^2}{1-\theta} \left(\frac{RT}{V} \right)^2 \quad (5)$$

Using the CSD conditions and assuming 0.100 g tetralin, 0.900 g 1-methylnaphthalene and a 1 atm N_2 atmosphere (0.0512 g), the result is

$$\theta = 0.9917$$

(ideal gas)

$$P = 12.32 \text{ atm}$$

The above calculation can be improved by using a more realistic equation of state such as the Redlich-Kwong equation (45). The calculation then becomes a two-step iterative process, involving Eq. (3) and the Redlich-Kwong equation solved for P .

$$P = \frac{RT}{\bar{V}-b} - \frac{a}{T^{1/2} \bar{V}(\bar{V}+b)} \quad (6)$$

In the above $\bar{V} = V/n$. The system of interest involves 5 components. Mixing rules must be used to calculate a and b . The following empirical rules are used:

$$b = \sum_i y_i b_i \quad (7)$$

$$a = \sum_i \sum_j y_i y_j a_{ij} \quad (8)$$

where

$$b_i = \frac{0.0867 R T_{ci}}{P_{ci}} \quad (9)$$

$$a_{ij} = \frac{0.4278 R^2 T_{cij}^{2.5}}{P_{cij}} \quad (10)$$

$$T_{cij} = (T_{ci} T_{cj})^{1/2} \quad (11)$$

$$P_{cij} = \frac{Z_{cij} R T_{cij}}{V_{cij}} \quad (12)$$

$$Z_{cij} = \frac{Z_{ci} + Z_{cj}}{2} \quad (13)$$

$$V_{cij} = \left(\frac{V_{ci}^{1/3} + V_{cj}^{1/3}}{2} \right)^3 \quad (14)$$

V_{ci} , T_{ci} , P_{ci} and Z_{ci} are, respectively, the pure-component critical volume, temperature, pressure and compressibility of component i .

The critical properties are taken from Reid and Sherwood (46).

Table 18. Critical Properties

Component	Subscript	V_c (cm ³ /mole)	Z_c	T_c (K)	P_c (atm)
Tetralin	1	438.0	0.246	716.5	33.05
Naph.	2	410	0.267	748.4	40.0
H ₂	3	65.0	0.305	33.2	12.8
1-Methylnaph.	4	462.0	0.257	772.0	35.2
N ₂	5	89.5	0.290	126.2	33.5

The values of b_i are calculated from Eq. (9).

$$b_1 = 154.2$$

$$b_2 = 133.1$$

$$b_3 = 18.5$$

$$b_4 = 156.0$$

$$b_5 = 26.8$$

From Eqs. (10), (11), (12), (13) and (14), the parameters a_{ij} , T_{cij} , P_{cij} , Z_{cij} and V_{cij} are calculated (Table 19).

The y_i values are calculated from the following equations:

$$y_1 = y_T = \frac{1-\theta}{1+2\theta+r} \quad (15)$$

$$y_2 = y_N = \frac{\theta}{1+2\theta+r} \quad (16)$$

$$y_3 = y_{H_2} = \frac{2\theta}{1+2\theta+r} \quad (17)$$

$$y_4 = \frac{n_{MN}/n_I}{1+2\theta+r} \quad (18)$$

$$y_5 = \frac{n_{N_2}/n_T}{1+2\theta+r} \quad (19)$$

In the above, n_{MN} = moles of 1-methylnaphthalene, n_{N_2} = moles of N_2 and $r = n_I/n_T = (n_{MN} + n_{N_2})/n_T$.

To initiate the calculation, the θ value from the ideal gas assumption is used. The y_i values are

$$\begin{aligned} y_1 &= 0.0006026 & y_2 &= 0.0720 \\ y_3 &= 0.1440 & y_4 &= 0.6077 \\ y_5 &= 0.1757 \end{aligned}$$

Table 19. Redlich-Kwong Calculated Parameters

ij	V_{cij} (cm ³ /mole)	Z_{cij}	T_{cij} (K)	P_{cij}	a_{ij} (x10 ⁻⁹)
11	438.0	0.246	716.5	33.05	1.198
12	423.8	0.257	732.3	36.4	1.148
13	195.9	0.275	154.2	17.8	0.048
14	449.9	0.251	743.7	34.0	1.278
15	219.7	0.268	300.7	30.1	0.150
22	410.0	0.267	748.4	40.0	1.104
23	187.6	0.286	157.6	19.7	0.046
24	435.5	0.262	760.1	37.5	1.224
25	210.8	0.279	307.3	33.4	0.143
33	65.0	0.305	33.2	12.8	0.0014
34	202.8	0.281	160.1	18.2	0.051
35	76.6	0.297	64.7	20.6	0.0047
44	462.0	0.257	772.0	35.2	1.355
45	227.2	0.273	312.1	30.8	0.161
55	89.5	0.290	126.2	33.5	0.015

The quantities b and a are calculated from Eqs. (7) and (8):

$$b = 111.8 \qquad a = 0.6629 \times 10^9$$

The total number of moles, n , is given by

$$\begin{aligned} n &= n_T (1 + 2\theta + r) \\ &= 0.01042 \text{ mole} \end{aligned} \qquad (20)$$

Assuming the volume to be 46.0 cm^3 ,

$$\bar{V} = \frac{V}{n} = 4415 \text{ cm}^3/\text{mole}$$

Applying the Redlich-Kwong equation and then Eq. (3),

$$P = 11.36 \text{ atm} \qquad (\text{Redlich-Kwong})$$

$$\theta = 0.9929$$

The calculation process can then be continued to convergence. The agreement between the first cycle Redlich-Kwong results and those from the ideal gas equation is regarded as adequate.

APPENDIX D

CALCULATION OF ELEMENTAL COMPOSITIONS OF VARIOUS
SYNTHETIC, HYDROGENATED CREOSOTE OILS

The CHN data on the hydrogenated creosote oils (Table 4) can readily be compared with the predicted elemental compositions of synthetic, hydrogenated creosote oils.

Table 20 presents the data of Burke et al. (29), on a GC/MS analysis of Allied 24-CB creosote oil. A synthetic creosote oil (Table 21) based upon the ten most abundant components of creosote oil as determined by Burke is used for the calculations. The % ion abundance of Table 20 is assumed to be equivalent to wt %. The wt % values of Table 21 are the % ion abundances of the first ten components of Table 20 normalized to 100%.

Four different model solvents based on the synthetic creosote oil are used for the calculations. The first solvent is the synthetic creosote oil of Table 21 and is designated as the unsaturated, synthetic creosote oil. The second solvent, the one-ring saturated, synthetic creosote oil, has one six-member ring saturated for every component of the unsaturated oil. The third solvent is the two-ring saturated, synthetic creosote oil with two six-membered rings saturated. The fourth solvent, the saturated, synthetic creosote oil, has all components completely saturated. Tables 22-25 indicate the component structural formulas and elemental percentages for all the synthetic solvents.

The calculated elemental contents for the synthetic solvents are shown in Table 26. The experimental values for creosote oil are $6.38 \pm 0.01\%$ H, $90.71 \pm 0.07\%$ C and $1.17 \pm 0.04\%$ N (Table 4). The values agree fairly well with those calculated for the unsaturated synthetic oil: 6.35% H, 92.70% C, 0.30% N and 0.65% O.

Table 20. GC/MS Analysis of Allied 24-CB Creosote Oil

Compound	Ion Abundance, %
Methylnaphthalene	22.0
Naphthalene	16.8
Acenaphthene	9.9
Phenanthrene	9.8
Fluorene	6.0
Dibenzofuran	5.8
C ₂ -Naphthalene	4.8
Biphenyl	4.2
Fluoranthene	3.7
Quinoline	2.4
Pyrene	2.2
Methyldibenzofuran	1.6
Cyclopentaphenanthrene	1.3
Methylphenanthrene	1.2
Benzindan	1.1
Dibenzothiophene	1.0
Anthracene	0.9
Methylacenaphthene	0.5
Dihdropyrene	0.4
Methylquinoline	0.3

* Taken from Ref. (29).

Table 21. Synthetic Creosote Oil

Compound	Structure	Wt %
Methylnaphthalene		25.76
Naphthalene		19.67
Acenaphthene		11.59
Phenanthrene		11.48
Fluorene		7.03
Dibenzofuran		6.79
Ethylnaphthalene		5.62
Biphenyl		4.92
Fluoranthene		4.33
Quinoline		2.81

Table 22. Component Elemental Compositions of Unsaturated, Synthetic Creosote Oil

Compound	Formula	MW	H, wt %	C, wt %	O, wt %	N, wt %
$C_{11}H_{10}$	142.20	7.09	92.91
$C_{10}H_8$	128.19	6.30	93.70
$C_{12}H_{10}$	154.21	6.54	93.46
$C_{14}H_{10}$	178.24	5.65	94.34
$C_{13}H_{10}$	166.23	6.06	93.93
$C_{12}H_8O$	168.21	4.79	85.69	9.51	

Table 22, continued

Compound	Formula	MW	H, wt %	C, wt %	O, wt %	N, wt %
$C_{12}H_{12}$	156.23	7.74	92.26
$C_{12}H_{10}$	154.21	6.54	93.46
$C_{16}H_{10}$	202.26	4.98	95.01
C_9H_7N	129.16	5.46	83.69		10.84

Table 23. Component Elemental Compositions of One-Ring Saturated, Synthetic Creosote Oil

Compound	Formula	MW	H, wt %	C, wt %	O, wt %	N, wt %
$C_{11}H_{14}$	146.23	9.65	90.35
$C_{10}H_{12}$	132.20	9.15	90.85
$C_{12}H_{14}$	158.24	8.92	91.08
$C_{14}H_{12}$	180.25	6.71	93.29
$C_{13}H_{16}$	172.27	9.36	90.64
$C_{12}H_{14}O$	174.24	8.10	82.72	9.18	

Table 23, continued

Compound	Formula	MW	H, wt %	C, wt %	O, wt %	N, wt %
$C_{12}H_{16}$	160.26	10.06	89.94
$C_{12}H_{16}$	160.26	10.06	89.94
$C_{16}H_{14}$	206.29	6.84	93.16
$C_9H_{11}N$	133.19	8.32	81.16		10.52

Table 24. Component Elemental Compositions of Two-Ring Saturated, Synthetic Creosote Oil

Compound	Formula	MW	H, wt %	C, wt %	O, wt %	N, wt %
$C_{11}H_{20}$	152.28	13.24	87.76
$C_{10}H_{18}$	138.25	13.12	86.88
$C_{12}H_{20}$	164.29	12.27	87.73
$C_{14}H_{18}$	186.30	9.74	90.26
$C_{13}H_{22}$	178.32	12.43	87.56
$C_{12}H_{20}O$	180.29	11.18	79.94	8.87	

Table 24, continued

Compound	Formula	MW	H, wt %	C, wt %	O, wt %	N, wt %
$C_{12}H_{22}$	166.31	13.33	86.67
$C_{12}H_{22}$	166.31	13.33	86.67
$C_{16}H_{20}$	212.33	9.49	90.51
$C_9H_{17}N$	139.24	12.31	77.64		10.06

Table 25. Component Elemental Compositions of Saturated, Synthetic Creosote Oil

Compound	Formula	MW	H, wt %	C, wt %	O, wt %	N, wt %
$C_{11}H_{20}$	152.28	13.24	86.76
$C_{10}H_{18}$	138.25	13.12	86.88
$C_{12}H_{20}$	164.29	12.27	87.73
$C_{14}H_{24}$	192.34	12.58	87.43
$C_{13}H_{22}$	178.32	12.43	87.56
$C_{12}H_{20}O$	180.29	11.18	79.94	8.87	

Table 25, continued

Compound	Formula	MW	H, wt %	C, wt %	O, wt %	N, wt %
$C_{12}H_{22}$	166.31	13.33	86.67
$C_{12}H_{22}$	166.31	13.33	86.67
$C_{16}H_{26}$	218.38	12.00	88.00
$C_9H_{17}N$	139.24	12.31	77.64		10.06

Table 26. Elemental Compositions for Hydrogenated Synthetic Creosote Oils

Syn. Creosote Oil	H, wt %	C, wt %	O, wt %	N, wt %
Unsaturated	6.35	92.70	0.65	0.30
One-Ring Saturated	8.89	90.19	0.62	0.30
Two-Ring Saturated	12.33	86.79	0.60	0.28
Saturated	12.76	86.35	0.60	0.28

APPENDIX E

CYCLOHEXENE HYDROGENATION, ISOMERIZATION AND
RECOVERY CALCULATIONS

Hydrogenation of cyclohexene/n-octane in the presence of kaolinite yields a variety of high boiling products which are not typically recovered in the liquid product used for GC analysis (Figure 17). Materials usually recovered include cyclohexene (I), cyclohexane (II), methylcyclopentane (III), 1-methylcyclopentene (IV), 3-methylcyclopentene (V), plus octane.

When interpreting the results of cyclohexene hydrogenation with mineral additives it is useful to define the quantities: percent hydrogenation, percent isomerization and percent recovery. This appendix describes how these quantities are defined.

All cyclohexene hydrogenations in this work involved an initial charge of one gram cyclohexene (0.01217 mole) plus three grams octane. A material balance on the products of a cyclohexene/octane hydrogenation with the additive kaolinite by vacuum fractionation indicated significant conversion of cyclohexene to high molecular weight products (Table 14). Near quantitative recovery (99.3%) of the octane was obtained, however.

In the following derivation it is assumed that octane is inert, and that no hydrocracking of octane or cyclohexene occurs. The concentrations of unreacted cyclohexene plus the products, II-V, are determined after hydrogenation by GC analysis using an internal standard.

Let R equal the recovered cyclohexene and its products expressed as cyclohexene, and let U equal the unrecovered cyclohexene. R and U are both in units of grams. The material balance condition requires that

$$1 = R + U \quad (1)$$

For any component i , the amount of that component recovered, R_i , is determined by the addition of an internal standard to an aliquot of the product solution.

$$R_i = \frac{m_S}{m_A} (4-U) \frac{A_i}{\rho_i} \quad (2)$$

m_S = mass of added standard

m_A = mass of aliquot of product solution

A_i = GC peak area ratio of component i relative to the standard

ρ_i = response factor of component i relative to the internal standard

The factor, $4-U$, included in Eq. (2) accounts for the four grams of cyclohexene plus octane charged to the reactor less the unrecovered cyclohexene, U .

In terms of the component values

$$\begin{aligned} R &= \sum_{i=1}^V R_i \frac{MW_I}{MW_i} \\ &= \frac{m_S}{m_A} (4-U) \sum_{i=1}^V \frac{A_i}{\rho_i} \frac{MW_I}{MW_i} \end{aligned} \quad (3)$$

Eq. (3) is substituted in Eq. (1) and the result solved for U .

$$U = \frac{1 - 4 \frac{m_S}{m_A} \sum_{i=1}^V \frac{A_i}{\rho_i} \frac{MW_I}{MW_i}}{1 - \frac{m_S}{m_A} \sum_{i=1}^V \frac{A_i}{\rho_i} \frac{MW_I}{MW_i}} \quad (4)$$

Finally, one defines

$$\text{Recovery, wt \%} = 100 \frac{(1-U)}{1g}$$

$$\text{Hydrogenation, mole \%} = \frac{100}{(0.01217 \text{ mole})} \left(\frac{R_{II}}{MW_{II}} + \frac{R_{III}}{MW_{III}} \right)$$

$$\text{Isomerization, mole \%} = \frac{100}{(0.01217 \text{ mole})} \left(\frac{R_{III}}{MW_{III}} + \frac{R_{IV}}{MW_{IV}} + \frac{R_V}{MW_V} \right)$$

Table 27 lists the response factors measured for the cyclohexene hydrogenation components relative to n-heptane.

Table 27. GC Response Factors for Cyclohexene Hydrogenation Components Relative to n-Heptane*

Component	Response Factor, ρ_i
Cyclohexene	1.1776
Cyclohexane	1.2108
Methylcyclopentane	1.1800
1-Methylcyclopentene	1.0093
3-Methylcyclopentene	1.1458

*The confidence level exceeds .994 for all ρ_i .

APPENDIX F

 ^{13}C -NMR SPECTRA FOR SELECTED SOLVENTS

Figure 18. ^{13}C -NMR Spectrum of Creosote Oil

Figure 19. ^{13}C -NMR Spectrum of CO-3

Figure 20. ^{13}C -NMR Spectrum of CO-24

Figure 21. ^{13}C -NMR Spectrum of CO-48

Figure 22. ^{13}C -NMR Spectrum of LR0-1

Figure 23. ^{13}C -NMR Spectrum of LRO-3

Figure 24. ^{13}C -NMR Spectrum of the Mobil Synthetic Solvent