Energy

F
O
S
S
I
L

240
10/9/84
(LB)

(1)

DR-0459-6

DOE/PC/30209-T7
(DE84014513)

SOLVENT TAILORING IN COAL LIQUEFACTION

Quarterly Report for the Period October—December 1983

By
A. R. Tarrer
Christine W. Curtis
James A. Guin
Dennis C. Williams

Work Performed Under Contract No. FG22-80PC30209

Auburn University
Auburn University, Alabama

Technical Information Center
Office of Scientific and Technical Information
United States Department of Energy

DISCLAIMER

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

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

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

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Printed Copy A03
Microfiche A01

Codes are used for pricing all publications. The code is determined by the number of pages in the publication. Information pertaining to the pricing codes can be found in the current issues of the following publications, which are generally available in most libraries: *Energy Research Abstracts (ERA)*; *Government Reports Announcements and Index (GRA and I)*; *Scientific and Technical Abstract Reports (STAR)*; and publication NTIS-PR-360 available from NTIS at the above address.

SOLVENT TAILORING IN COAL LIQUEFACTION

Quarterly Report for the Period
October, 1983 - December, 1983

A. R. Tarrer
Christine W. Curtis
James A. Guin
Dennis C. Williams

Coal Conversion Laboratory
Auburn University
Department of Chemical Engineering
Auburn University, AL 36849

MASTER

PREPARED FOR THE UNITED STATES DEPARTMENT OF ENERGY

Under Contract No. DEFG2280PC30209

Objective. The objective of this project is to identify the mechanisms whereby the solvent functions during coal liquefaction to allow tailoring of the process solvent composition for improved coal dissolution and processing. The role of hydrogen donation is important in coal liquefaction. Aromatic and aliphatic solvents do not generally transfer hydrogen to coal, but the hydroaromatic compounds contained in the process solvent are important factors in coal dissolution. The contribution of transferable hydrogen to coal dissolution must be quantitatively determined in order to effectively tailor a process solvent for maximal effectiveness during liquefaction.

Summary of Previous Work. The contribution of transferable hydrogen in coal-derived solvents to coal conversion was investigated in a two-step process. Initially, the amount of transferable hydrogen in the coal-derived solvents was analyzed by spectroscopic methods and by catalytic dehydrogenation. The spectroscopic methods included carbon magnetic resonance, proton magnetic resonance as well as a combination of these two methods. Three of the methods gave nearly equivalent quantities for the amount of transferable hydrogen present in the complex coal liquids. Coal conversion determined in each of the coal-derived solvents was correlated to the amount of transferable hydrogen present. The contribution of transferable hydrogen is a significant factor in coal dissolution and the presence of saturates and hexane insolubles compounds in these solvents may have a detrimental effect on coal dissolution.

Work Done During This Quarter. A significant amount of time has been spent in revising the manuscript "Contribution of Transferable Hydrogen to Coal Conversion". This manuscript has been accepted for publication in Fuel. A copy of the manuscript follows.

A major question and point of contention among the reviewers concerned the method of catalytic dehydrogenation as a legitimate method for quantifying the amount of donable hydrogen present in the process solvent. The catalytic dehydrogenation method does have its limitations as are carefully and clearly stated in the manuscript. These limitations, however, are no greater than those encountered by other commonly accepted spectroscopic techniques for measuring donable hydrogen. Several of the reviewers asked for more in-depth description of the method of catalytic dehydrogenation which was added to the manuscript.

CONTRIBUTION OF TRANSFERABLE HYDROGEN
TO COAL CONVERSION

Christine W. Curtis

James A. Guin

Michael A. Hale

Nelson L. Smith

Auburn Coal Conversion Laboratory
Chemical Engineering Department
Auburn University
Auburn, Alabama

Abstract

The contribution of transferable hydrogen in coal-derived solvents to coal conversion was investigated in a two-step process. Initially, the amount of transferable hydrogen in the coal-derived solvents was analyzed by spectroscopic methods and by catalytic dehydrogenation. The spectroscopic methods included carbon magnetic resonance, proton magnetic resonance as well as a combination of these two methods. Three of the methods gave nearly equivalent quantities for the amount of transferable hydrogen present in the complex coal liquids. Coal conversion determined in each of the coal-derived solvents was correlated to the amount of transferable hydrogen present. The contribution of transferable hydrogen is a significant factor in coal dissolution and the presence of saturates and hexane insolubles compounds in these solvents may have a detrimental effect on coal dissolution.

Introduction

The ability of hydroaromatic compounds to dissolve coal during liquefaction has been demonstrated by many researchers.¹⁻⁵ It is well known that hydroaromatic compounds in comparison to their aromatic analogs show increased coal dissolution. Recent studies have developed spectroscopic techniques to measure the hydroaromaticity of complex coal liquids.⁶⁻⁸ These methods, for the most part, are based on nmr spectral windows derived from model compound studies. Coal-derived liquids which have been shown to contain hydroaromatic compounds, in most cases, provide effective coal dissolution solvents. The primary objective of this work is to determine the amount of donable hydrogen in coal-derived liquids and the relationship of this factor to coal conversion during liquefaction. This objective is achieved by quantitatively measuring the donable hydrogen in a series of hydrogenated creosote oils, in coal-derived recycle solvents and in synthetic model compound solvents and correlating their hydrogen donor concentration with the conversion of Western Kentucky 9/14 coal at typical liquefaction conditions. In this study, hydroaromaticity of the coal liquids is measured by four methods: (1) proton magnetic resonance (¹HNMR), (2) carbon-13 magnetic resonance (¹³CMR), (3) a combination of ¹HNMR and ¹³CMR and (4) catalytic dehydrogenation of the solvents.

For this investigation, a series of hydrogenated creosote oils prepared by catalytic hydrotreatment were used as solvents for coal dissolution. Recycle solvents derived from bituminous coals at the Wilsonville Advanced Coal Liquefaction Research and Development Facility, a synthetic solvent composed

of four model compounds, and selected model compounds were also used in a similar way. The hydroaromaticity of these solvents was obtained by both spectroscopic methods and catalytic dehydrogenation thus yielding the amount of transferable hydrogen present in the coal liquids. In addition, to avoid a larger estimate of transferable hydrogen than exists in each of these methods, the saturated compounds were removed chromatographically from the whole oils prior to analysis. The coal liquids were subsequently separated into aromatic and polar fractions, each of which was examined for hydroaromaticity. The amount of transferable hydrogen determined by each of the four methods was then compared with the ability of each solvent to convert coal to cresol solubles.

Experimental

Dissolution Experiments

The solvents used in this study were creosote oil, a series of hydrogenated creosote oils, two coal-derived recycle solvents and other model compounds, including 2, 3, and 4-ring hydroaromatic and aromatic compounds and saturated hydrocarbons. A synthetic solvent composed of 2% 4-picoline, 17% p-cresol, 43% tetralin and 38% 1-methylnaphthalene modeled after the solvent developed by researchers at Mobil was also used.⁹ The creosote oil (CO), obtained from Southern Company Services, Inc., was hydrogenated in a 300 ml autoclave using a presulfided CoMo/Al₂O₃ catalyst, a hydrogen atmosphere of ~2000 psig at reaction conditions and reaction times of 3, 12, 24 and 48 hours. The method of preparation is described in detail in a previous work.¹⁰ The recycle oils, obtained from the Wilsonville Advanced Coal Liquefaction Research and Development Facility, were derived from Kentucky 9 (Lafayette mine) coal (RO-1) and Indiana V coal (RO-3). Elemental analyses of all coal-

derived solvents used are given in Table 1. The notation for the creosote oils is such that the numbers after the dash indicate the number of hours of hydrogenation. Coal dissolution experiments were conducted with Western Kentucky 9/14 coal of -20 to +270 mesh in 15 cc stainless steel microreactors.¹¹ An elemental analysis of Western Kentucky 9/14 coal is presented in Table 2. Reaction conditions for these experiments were: 2.5 g coal, 5.0 g solvent, air at 1 atmosphere, reaction temperature of 410°C, agitation rate of 860 rpm, and 30 minutes reaction time. Experiments performed with N₂ yielded the same coal conversion; therefore, no attempt was made to remove the air. Coal conversion was determined by ashing of hot cresol insolubles.

Chromatography

A Waters Associates liquid chromatograph equipped with a Valco 7000 psig injection valve, an R-401 differential refractometer, and a Schoeffel SF 770 UV detector set at 267 nm was used to separate the hexane soluble portion of the coal liquids into saturate, aromatic and polar fractions. The samples were separated using a precolumn which had been dry packed with 20-44 μ Bio-Sil A followed by two 1 cm i.d. x 50 cm columns which had been slurry packed with 20-44 μ Bio-Sil A and activated by heating overnight at 105°C in dry nitrogen. The coal liquids were eluted with hexane at a flow rate of 8.2 ml/min to separate the saturate and aromatic fractions and with a 50:50 mixture of methylene chloride:acetone to remove the polar fraction from the column. The column was washed with methylene chloride before the next separation. Calibration was accomplished with model compounds.

Catalytic Dehydrogenation

The coal-derived liquids (sample sizes ranging from 0.1 to 0.4 g) were catalytically dehydrogenated using 0.3 g of a 5 wt% Pd on CaCO_3 catalyst in a sealed microreactor for four hours. The reactor was purged with nitrogen prior to reaction. The reaction on the neat coal-derived liquids was performed at 390°C with an agitation rate of 600 cpm. The quantity of gas produced was measured by means of a gas buret as shown in Figure 1 and the composition of gas, by gas chromatography using a packed microsieve column and thermal conductivity detection. The conditions for the catalytic dehydrogenation of coal-liquids was determined by performing catalytic dehydrogenation on a binary system of 10 to 30 wt% model compound in 1-methylnaphthalene with a 1 g total charge. Model compounds including saturates, hydroaromatics and aromatics were used to test the method. Under these reaction conditions, 1-methylnaphthalene does not readily dehydrogenate. In fact, as the mole fraction of H_2 generated from the hydroaromatics increases in the reactor the amount of 1-methylnaphthalene dehydrogenating becomes very small as shown in Figure 2. The optimal reaction time for the catalytic dehydrogenations was selected by determining the amount of time required for ~100% dehydrogenation of hydroaromatic hydrogens in hydroaromatic compounds using a number of model compounds.

Magnetic Resonance Spectroscopy

An 80 MHz Varian CFT-20 spectrometer with a 620/L computer operated with noise decoupling was used to determine the ^{13}C spectra of the coal-derived liquids. The parameters for each analysis follow: ambient temperature; acquisition time, 1.024 s; spectral width, 4000 Hz; pulse width, 7 μs ; flip angle, 30° ; and delay time between individual pulses, 100 s. The long delay times were employed to allow carbons with long T_1 relaxation times sufficient

time to reach equilibrium before the next pulse was started to aid in accurate quantitation of all types of carbon atoms. The decoupler was on during data acquisition and off during pulse delays to minimize NOE effects. For both model solvents and coal liquids, 1.5 g of sample in 2.4 g of deuterated CHCl_3 with TMS as an internal standard was used. The ^1H NMR spectra of the coal-derived liquids were obtained using a Varian EM-390 with samples being dissolved in CDCl_3 and using TMS as an internal standard.

Results and Discussion

Coal dissolution experiments performed with the whole coal-derived solvents yielded maf coal conversions to cresol solubles ranging from 19.1% for creosote oil to 86.4% for C0-24, a creosote oil which has undergone hydrogenation for 24 hours. Coal conversion for the coal-derived solvents as a function of their respective hydrogen contents is shown in Figure 3. Coal conversion only correlated with the hydrogen content of the hydrogenated creosote oils up to a certain level. Oversaturation can occur as in C0-48, producing a solvent less suited for coal dissolution and resulting in decreased coal conversion. The recycle solvents with hydrogen contents of 8.45% to 9.20% produced lower coal conversion than did creosote oils of comparable hydrogen contents. The differences in coal conversion with equivalent hydrogen contents illustrate the fact that it is the type of hydrogen in addition to the total hydrogen content that is an important factor in coal dissolution. The lack of hydroaromatics in such solvents as the original creosote oil and aromatic and saturated model compounds resulted in low, <30%, coal conversions, while solvents containing hydroaromatics such as the synthetic solvent and tetralin increased coal dissolution yields to 62.3% and 71.8%.

This lack of direct correlation between total hydrogen content and coal dissolution and the fact that the presence of hydroaromatics is beneficial for coal conversion provided the motivation for the remainder of this work. The emphasis of this work is to determine the hydroaromaticity in complex coal solvents and to relate this factor to coal conversion. Spectroscopic techniques developed by other researchers⁶⁻⁸ have been modified to some extent and then applied to a series of coal-derived liquids. A method for determining the hydroaromaticity of liquids by catalytic dehydrogenation has also been developed and applied to coal-derived liquids.

The determination of hydroaromaticity of coal-derived solvents is difficult due to the complexity and large variety of compounds present. The four techniques used carbon magnetic resonance (¹³CMR), proton magnetic resonance (¹HNMR), a combination of ¹HNMR and ¹³CMR and catalytic dehydrogenation, are the most promising methods available for determining hydroaromaticity of coal-derived liquids, but each still has inherent problems. The use of a single compound as a model acceptor and a test for hydrogen donor ability has been shown to give variable and at times misleading results when compared to actual coal dissolution data.¹² In each method used in this study, the major inaccuracy in predicting hydroaromaticity results from the presence of saturated compounds which leads to a higher level of hydroaromaticity than is actually present. In the NMR methods, absorptions due to the saturated compounds appear in the region of interest; during catalytic dehydrogenation hydrogens can be stripped from the saturates producing a larger hydrogen yield than that available solely from the hydroaromatics. To circumvent this problem, the hexane soluble fraction of selected coal liquids was chromatographically separated, using the method

developed by Suatoni and Swab¹³⁻¹⁴, into saturate, aromatic and polar fractions, thereby removing the interference produced by the saturates from the hydroaromaticity measurement. The solvents containing appreciable amounts of hexane insolubles were creosote oil, 6.5%; RO-1, 4.2%; and RO-3, 4.7%. A complete breakdown of the saturate, aromatic and polar fractions present in each coal-derived solvent is given in Figure 4. The creosote oils contained less than 3.0% saturates with the exception of CO-48 which contained ~21%. Recycle oils, RO-1 and RO-3, contained 10% and 11% saturates, respectively. The solvents with more than 10% polars included CO-3 with 13.5%, the original creosote oil, CO, 19.8%, RO-1, 34.8%, and RO-3, 40.9%. The completeness of the separation was verified by ¹HNMR which showed no aromatic hydrogen present in the aliphatic fraction. Hydroaromatics are present in both the aromatic and polar fractions as evidenced by the presence of both cyclic alpha and beta protons.

Catalytic Dehydrogenation

The catalytic dehydrogenation of coal-derived solvents is based upon earlier work performed by Raymond, Wender and Reggel on the catalytic dehydrogenation of coal.¹⁵⁻¹⁸ In their work, coal vitrains were catalytically dehydrogenated using palladium on calcium carbonate in boiling phenanthridine in a helium atmosphere and the evolved gases were measured. The gases evolved consisted primarily of hydrogen with small amounts of carbon monoxide, carbon dioxide, nitrogen, methane, and other hydrocarbons being present. Further application of their technique showed that coal could act either as a donor or an acceptor of hydrogen depending upon its rank and that different coal macerals yielded different hydrogen contents. In this work, their method has been adapted to apply to liquids. The details of the procedure are given in

the experimental section. The validity of the method was established by the catalytic dehydrogenation of model compounds in the presence of a diluent solvent, 1-methylnaphthalene. The hydrogen yield and the reaction products obtained from these model compound experiments are shown in Table 3. The evolved gases from the model compounds were all greater than 99% hydrogen. The main problem which became apparent through the catalytic dehydrogenation of these model compounds was the propensity of saturated compounds and alkyl sidechains to dehydrogenate. Since the hydrogen evolved from the saturated compounds is not considered to be donable during coal liquefaction processing, an overprediction of transferable hydrogen from hydroaromatics would result. This problem is best circumvented by removing the saturates from the coal liquids prior to catalytic dehydrogenation.

Chromatographically separated fractions of the coal liquids were catalytically dehydrogenated. The mole percent of hydrogen evolved ranged from 50.9% to 96.6%; other prominent gases included CH₄, C₂H₄, C₃H₆, C₃H₈, H₂S and CO₂. As the hydrogen content of the hydrogenated creosote increased, the amount of hydrogen evolved also increased. Hydrogen yields for the coal-derived liquids used in this study are given in Table 4. Creosote oil and the recycle oils produced the largest amount of H₂S since they had not undergone catalytic hydrogenation, a process which removes the organic sulfur from the oils.

Magnetic Resonance

¹³CMR spectra were obtained for the aromatic fraction of each selected coal liquid and also for the polar fraction of the recycle oils. The synthetic solvent was used as a standard to establish the validity of the instrumental parameters. Two hydroaromatic windows in the ¹³CMR were selected:

(1) 22 - 31 ppm as defined by Seshadri⁶ and (2) 22.5 - 37 ppm as defined by Snape⁷. Seshadri and coworkers examined the chemical shifts of a number of model hydroaromatic solvents along with aromatic fractions of hydrogenated coal-derived solvents. They concluded that the saturated carbons of the hydroaromatic species fall within the ppm range of 22 - 31 ppm relative to TMS. Based upon a survey of ¹³C chemical shifts obtained from numerous sources, Snape et al⁷ proposed a wider hydroaromatic window of 22.5 to 37.0 ppm. Although the narrower range described by Seshadri may exclude some resonances of hydroaromatic species such as the CH₂ resonance of dihydroanthracene at 37.7 ppm, the broader range given by Snape may include a larger number of interferences such as of alkyl sidechains on aromatic compounds. Fewer interferences are expected in both regions when the saturates are chromatographically removed prior to ¹³CMR analysis. Integrals for the hydroaromatic carbons were measured over the two windows and for aromatic carbons over the 100-148 ppm region. Standard values were obtained using the synthetic solvent which gave good agreement between the theoretical and ¹³CMR determined integrals. Comparison of the aromaticities, f_a , obtained by ¹³CMR and by the Brown-Ladner equation also showed fairly good agreement as shown in Table 5. The Brown-Ladner equation predicts a uniformly decreasing f_a as the extent of hydrogenation is increased in the hydrogenated creosote oils. The ¹³CMR data show the same trend except for two small anomalies observed in the C0-24 whole oil and in the C0-3 aromatic fraction. These anomalies in the ¹³CMR data most probably result from an inadequate signal to noise ratio due to instrument time limitations resulting from insufficient scans as well as difficulty in phase adjustment on some samples.

Proton magnetic resonance was used to determine hydroaromaticity according to the method described by Burke¹⁹. The principal hydroaromatic regions include (1) 4.6 to 2.5 ppm which corresponds to cyclic alpha protons and (2) 2.0 to 1.4 ppm for the cyclic beta protons. The cyclic beta region includes saturated ring structures, making use of the coal liquids' aromatic fraction rather than the whole oil desirable. A combined ¹³CMR and ¹HNMR method similar to the one developed by Clarke⁸ was also used in this study. Clarke's method uses ¹HNMR of a whole coal liquid to make an estimation of donable hydrogen and then utilizes ¹³CMR spectra to subtract from this value interferences caused by saturates and alkyl substituents associated with the aromatics.

Calculation of Transferable Hydrogen

The objective of this work is to determine the amount of transferable hydrogen; that is, the amount of hydrogen donable from the hydroaromatic species in the coal-derived solvent to coal during liquefaction. The amount of transferable hydrogen can be estimated from the data obtained by the four abovementioned techniques. In applying these techniques, it is assumed that all of the transferable hydrogen is contained in the aromatic fraction of the solvents, except for the recycle oils, where the polar fraction is also considered.

Calculation of the transferable hydrogen by catalytic dehydrogenation assumes, based upon the model compound study, that hydrogen is evolved from the hydroaromatic species alone, in other words, from no other species and that none is consumed in the formation of hydrocarbon gases or H₂S. The transferable hydrogen, H_D, of the whole creosote oils is calculated by,

$$H_D (\text{wt}\%) = \frac{[(H_{2(g)}) \text{ ml/g solvent} (\text{wt}\% \text{ Ar fraction}) (2.1058 \text{ g/mole})]}{22,414 \text{ ml/mole}} \quad (1)$$

where wt% Ar fraction denotes the weight percent of aromatics obtained from the total oil by chromatographic analysis. For the recycle oils, transferable hydrogen is calculated from the hydrogen evolved from both the polar as well as the aromatic fraction.

Transferable hydrogen can be obtained from the ^{13}CMR data by basing the calculation on the integrals obtained from the previously mentioned hydroaromatic windows of the coal-derived liquids. The donable hydrogen is calculated by,

$$H_D (\text{wt}\%) = \frac{\left[\left(\frac{H_A}{C_T} \right) 100 (\text{wt}\% \text{ Ar fraction}) (\text{wt}\% \text{ C in Ar fraction}) (1.0079) \right]}{12.001 \times 10^4} \quad (2)$$

where, H_A = hydroaromatic window integral; C_T = ^{13}CMR integral for 11-60 and 100-168 ppm which corresponds to the total amount of carbon in the sample. The 10^4 in the denominator is to eliminate the 10^4 arising from the weight percents present in the numerator. As before, the recycle solvents' transferable hydrogen is calculated for both the aromatic and polar fractions. Even with the removal of the saturates from these calculations, some interferences may remain due to alkyl sidechains on aromatic species and to aromatic species with saturated five-membered rings. Even with these interferences, the overwhelming majority of carbons in the windows used can be attributed to hydroaromatic species.

Transferable hydrogen calculated by $^1\text{H NMR}$ uses the sum of the cyclic alpha (H_α) and the cyclic beta (H_β) protons and total hydrogen (H_T) as given

below:

$$H_D \text{ (wt\%)} = \frac{\frac{[H_\alpha + H_\beta] 100 \text{ (wt\% Ar fraction) (wt\% H in Ar fraction)}}{H_T}}{2 \times 10^4} \quad (3)$$

The two in the denominator accounts for the fact that only half of the hydrogen in the hydroaromatic region is transferable. The transferable hydrogen calculated for the coal-derived liquids based on the ^1H NMR spectrum of the whole oil and of the aromatic and polar fractions is given in Table 6.

Clarke et al⁸ calculated transferable hydrogen by combining ^{13}C MR and ^1H NMR techniques. The ^1H NMR of whole oils was used to make an estimation of H_D . From this estimation were subtracted the interferences caused by saturates and alkyl substituents on aromatic rings as determined by ^{13}C MR. In this work a combined ^{13}C MR and ^1H NMR method was also used to determine transferable hydrogen. Similarities exist between this method and the method of Clarke⁸; however, the terminology and ppm ranges have been changed. The saturates were removed chromatographically and analyzed by ^1H NMR. The combined method used to calculate transferable hydrogen is described below.

Proceeding generally along the same lines as Clarke, et al⁸, the concentration of donable hydrogen in hydroaromatic rings (H_D) is estimated by:

$$H_{D_1} = \frac{(H_\alpha + H_\eta - H_{C_1})}{n} \quad (4)$$

where,

H_α = wt% hydrogen in the 2.0 to 3.4 ppm range in the ^1H NMR spectrum of the whole oil

H_η = wt% hydrogen in the 1.4 to 2.0 ppm range in ^1H NMR spectrum of the whole oil

H_{C_1} = a correction factor for non-donor groups

n = the (H/C) atomic ratio of the hydroaromatic rings taken as 1.7 to 2.0.

H_{C_1} is determined by ^{13}CMR and consists of interferences caused by $\alpha\text{-CH}_3$ and $\alpha\text{-alkyl CH}_2$ found in the 18-22.5 ppm and 11-18 ppm regions, respectively. Three hydrogen atoms are associated with each methyl carbon and two with each methylene carbon. The number of $\alpha\text{-alkyl}$ carbons is assumed to equal the number of non $\alpha\text{-CH}_3$ carbons found using the CMR integral over the 11-18 ppm region, in that, terminal CH_3 groups are required for all alkyl sidechains and are assumed to correspond to the methylene groups present. It must be realized that this correspondence is an approximation. For example, for ethyl benzene the correspondence is one to one as assumed; however, for propylbenzene one methylene group is not counted, and for isopropyl over compensation occurs with two methyl groups being counted for one methine group. Interferences associated with hydrogens of saturated species can be determined by chromatographically removing the saturates and obtaining their $^1\text{HNMR}$ spectra and by determining their elemental analyses. A hydrogen mass balance can be made to subtract these interferences from the whole spectra.

$$H_{C_1} = \frac{(1.0079)[\% \alpha\text{-CH}_3 \text{ C}](3) + (\% \text{ non } \alpha\text{-CH}_3)(2)] (\text{wt\% C in whole oil})}{12.011 \times 10^2} \quad (5)$$

$$+ \frac{(\% \text{ of total H in 1.4-2.0 ppm region of saturates}) (\text{wt\% saturates in whole oil}) (\text{wt\% H in saturates fraction})}{1.0 \times 10^4}$$

The concentration of donable hydrogen in naphthene rings on hydroaromatic species such as 1,2,3,4,4a,9,10,10a octahydrophenanthrene (H_{D_2}) is estimated by

$$H_{D_2} = \frac{(H_{\beta} + H_{\gamma} - H_{C_2})}{n} \quad (6)$$

where,

$H_{\beta} + H_{\gamma}$ - wt% hydrogen in the 0.5 to 1.4 ppm region of the 1H NMR spectrum of the whole oil

H_{C_2} = a correction factor for non-donor hydrogen including

- (1) non α -CH₃ groups estimated using the 11-18 ppm ^{13}C MR integral
- (2) the $H_{\beta} + H_{\gamma}$ saturates calculated in the same manner as in H_{C_1} but using the 0.5 to 1.4 1H NMR integral

H_{C_2} , therefore, can be defined as:

$$H_{C_2} = \frac{(1.0079)[\% \text{ non } \alpha\text{-CH}_3 \text{ C.}](3)] (\text{wt\% C in whole oil})}{12.011 \times 10^2} \quad (7)$$

$$+ \frac{(\% \text{ of total H in 1.4-2.0 ppm region of saturates}) (\text{wt\% saturates in whole oil}) (\text{wt\% H in saturates fraction})}{1.0 \times 10^4}$$

The total donable hydrogen is obtained by summing H_{D_1} and H_{D_2} . The correction factors, H_{C_1} and H_{C_2} , are at best approximations. Considering the abovementioned assumptions with H_{C_1} and the impossibility of subtracting out all possible interferences from the 1H NMR of the whole oil, the combined ^{13}C MR and 1H NMR method will provide, in many cases, an upper limit to the amount of transferable hydrogen present.

A comparison of the amount of transferable hydrogen calculated by catalytic dehydrogenation, ^{13}CMR , cyclic alpha and beta hydrogen from $^1\text{HNMR}$ and the combined $^1\text{HNMR}$ - ^{13}CMR method is given in Table 7. Three methods of calculating transferable hydrogen, ^{13}CMR 22-31 ppm, $^1\text{HNMR}$, and catalytic dehydrogenation give values which correspond fairly closely. A parity plot of transferable hydrogen obtained from catalytic dehydrogenation to that obtained from the ^{13}CMR 22-31 ppm window is given in Figure 5. The excellent correspondence obtained indicates that both methods give comparable H_D values for both the hydrogenated creosote oils and the recycle oils. The other two methods, ^{13}CMR with a 22.5-37.0 ppm window and combined ^{13}CMR - $^1\text{HNMR}$ technique produced low values for solvents containing little donable hydrogen. In fact, the combined method was the only procedure which showed a definite difference in donable hydrogen in oils C0-24 and C0-48.

Some differences were observed among the values for transferable hydrogen determined by the methods shown in Table 7. The values for transferable hydrogen for a specific oil may differ by a factor of two with the recycle oils, R0-1 and R0-3, showing the most variation. Each method has its difficulties: (1) the ^{13}CMR range of 22 -31 ppm may exclude some carbons with hydroaromatic hydrogens attached to them, (2) the ^{13}CMR range of 22.5 -37 ppm may be too large including some carbons of aliphatic sidechains, (3) the $^1\text{HNMR}$ data includes the typical inaccuracies due to interferences, possible solvent shifts, etc. and (4) catalytic dehydrogenation may produce excess hydrogen.

Comparison of the transferable hydrogen obtained by the various methods for the synthetic solvent to the theoretical amount of 1.27 shows the values obtained have a relative error between 1.5% to 15% with the least accurate

method being $^1\text{HNMR}$. The accuracy of the various methods for the coal-derived solvents can not be absolutely determined. The accuracy depends upon the chemical composition of each solvent and the influence of the specific solvent's interferences on each method of determining transferable hydrogen. Determination of transferable hydrogen with a wider range of coal-derived solvents and comparison of the solvent's ability to convert coal may help delineate the applicability and range of accuracy of each technique.

Contribution of Transferable Hydrogen to Coal Conversion

Comparison of coal conversion to the amount of transferable hydrogen determined to be present in the hydrogenated creosote oils and the recycle solvents by ^{13}CMR (22-31 ppm), $^1\text{HNMR}$ (cyclic $\alpha + \beta$), catalytic dehydrogenation and the combined $^{13}\text{CMR} - ^1\text{HNMR}$ are given in Figures 6-9. For each of these methods, a general increase in the amount of coal conversion with increased transferable hydrogen is observed. Using the first three methods mentioned above, coal conversion for creosote oil, C0, is 19% with a low transferable hydrogen between 0.19 to 0.29 and for C0-24 a coal conversion of 86% is obtained with high transferable hydrogen between 1.24 and 1.31. For the highly hydrogenated C0-48 solvent, less coal conversion is obtained than for C0-24 with the amount of transferable hydrogen being nearly equivalent. The recycle solvents as well show lower coal conversion than the amount of transferable hydrogen present would indicate. For the combined ^{13}CMR and $^1\text{HNMR}$ method, the C0-24 oil yielded higher transferable hydrogen and higher coal conversion as compared to C0-48 which showed lower transferable hydrogen and lower coal conversion. In essence, the combined method is the only procedure which predicts the fall-off in transferable hydrogen when comparing C0-24 to C0-48 as the total hydrogen content and amount of saturates increase.

These results from the different methods of transferable hydrogen illustrate the complexity of coal-derived liquids and the numerous factors affecting coal conversion. As noted earlier, coal dissolution experiments were performed using the whole oils; CO-48 and the recycle oils each contained a substantial percentage of saturates and the recycle oils a significant amount of hexane insolubles and a higher level of heteroatoms. The presence of saturated compounds in a hydroaromatic solvent has been shown in model compound studies to decrease the amount of coal conversion.²⁰ Data obtained in this laboratory has shown that the conversion of a bituminous coal in a tetralin/aromatic solvent is quite different from that obtained in a tetralin/aliphatic solvent under identical reaction conditions. Thus, when coal was liquefied in a tetralin/1-methylnaphthalene system, 68% coal conversion was achieved; in contrast, in a tetralin/hexadecane system containing the same amount of tetralin, only 28% of the coal was converted. This evidence indicates that the presence of saturates in the coal liquefaction solvent may be detrimental to coal conversion and that other factors in addition to the amount of transferable hydrogen are important in coal conversion. Therefore, the fact that the whole oil CO-48 contains 21% saturates may account for the discrepancy between coal conversion and amount of transferable hydrogen. In the case of the recycle solvents the high percentage of polar and hexane insoluble compounds and their effect on coal dissolution must also be considered and is an area for further research. Even with these influences which may diminish the overall efficacy of the solvent to dissolve coal, it is apparent that the contribution of hydroaromatics in coal-derived solvents is an important factor for the solvolysis of coal.

Summary

This investigation applies spectroscopic techniques and a catalytic dehydrogenation technique for the determination of transferable hydrogen in complex coal liquids. Three of methods, ^{13}CMR using the 22-31 ppm window, $^1\text{HNMR}$ using cyclic alpha and beta protons, and catalytic dehydrogenation of the solvents provide comparable values for transferable hydrogen in creosote oil-derived solvent and in coal recycle solvents. The contribution of hydroaromaticity as based on donable hydrogen is a significant factor in coal dissolution. The results indicate that the presence of saturates and other compounds may have a detrimental effect on coal dissolution even when the amount of transferable hydrogen is nearly equivalent in different coal-derived solvents.

Acknowledgements

The authors gratefully acknowledge the support of the Department of Energy under Contracts DEAC2279ET13397 and DEFG2280PC30209 for this work.

References

1. Neavel, R. C., Fuel, 1976, 55, 237.
2. Guin, J. A., Curtis, C. W., and Kwon, K. C., Fuel, 1983, 62, 1412.
3. Furlong, M. W., Baldwin, Robert M. and Bain, R. L., Fuel, 1982, 61, 116.
4. Final Technical Report for the period January 1, 1976 - June 30, 1977, "EDS Coal Liquefaction Process Development, Phase III A", DOE Contract No. E (49-18) 2353, February, 1978.
5. Curtis, C. W., Guin, J. A., and Kwon, K. C., AIChE National Meeting, paper 62b, November, 1982.
6. Sheshadri, K. S., Raffaele, G. R., Douglas, M. J., and Malone, H. P., Fuel, 1978, 57, 549.
7. Snape, C. E., Ladner, W. D., and Bartle, W. D., Anal. Chem., 1979, 51, 2189.
8. Clarke, J. W., Rantell, T. D., and Snape, C. E., Fuel, 1982, 61, 707.
9. Whitehurst, D. D. and Mitchell, T. O., ACS Fuel Preprints, 1976, 21(5), 127.
10. Curtis, C. W., Guin, J. A., Jeng, J., and Tarrer, A. R., Fuel, 1981, 60, 677.
11. Curtis, C. W., Guin, J. A., Tarrer, A. R., and Huang, W. J., Fuel Processing Technology, 1983, 7, 277.
12. Curtis, C. W., Guin, J. A., and Kwon, K. C., Fuel, in press, 1984.
13. Suatoni, J. C. and Swab, R. E., J. Chrom. Sci., 1975, 13, 361.
14. Suatoni, J. C. and Swab, R. E., J. Chrom. Sci., 1976, 14, 535.
15. Raymond, R., Wender, I., and Reggel, L., Science, 1962, 137, 631.
16. Reggel, L., Wender, I., and Raymond, R., Fuel, 1968, 47, 373.
17. Reggel, L., Wender, I., and Raymond, R., Fuel, 1964, 43, 229.
18. Reggel, L., Wender, I., and Raymond, R., Fuel, 1970, 49, 281.
19. Burke, F. P., Winschel, P. A., Pochapsky, T. C., DOE Contract AC05-79ET14503, April, 1980.
20. Majlessi, H., Masters Thesis, Auburn University, 1981.

Table 1
Elemental Analysis of Coal-Derived Solvents

Solvent	H, Wt%	C, Wt%	N, Wt%
Creosote Oil (C0)	6.38 $\pm$ 0.01	90.71 $\pm$ 0.17	1.17 $\pm$ 0.04
C0-3	7.20 $\pm$ 0.18	90.56 $\pm$ 0.71	1.18 $\pm$ 0.38
C0-12	8.14 $\pm$ 0.09	90.35 $\pm$ 0.16	0.44 $\pm$ 0.05
C0-24	8.59 $\pm$ 0.18	89.37 $\pm$ 1.10	0.53 $\pm$ 0.35
C0-48	10.74 $\pm$ 0.11	89.13 $\pm$ 0.15	~ 0.00
Kentucky 9 (R0-1)	8.45 $\pm$ 0.12	87.38 $\pm$ 0.08	0.74 $\pm$ 0.05
Indiana V (R0-3)	9.20 $\pm$ 0.08	86.35 $\pm$ 0.03	0.72 $\pm$ 0.01

Table 2
Elemental and Proximate Analysis of Western Kentucky 9/14 Coal

Elemental Analysis, %		Proximate Analysis (wt%)	
C	88.1	VM	38.0
H	5.8	FC	53.0
N	1.3	ASH	8.9
O	9.5	MOISTURE	4.2
S	3.4		

Table 3
Catalytic Dehydrogenation of Model Compounds

Compound	Major Products	Moles H ₂ / Mole HA	Conversion, %
1,4-Dihydronaphthalene	Naphthalene	1	90.0 $\pm$ 0.3
1,2-Dihydronaphthalene	Naphthalene	1	90.9 $\pm$ 0.8
Tetralin	Naphthalene	2	89.9 $\pm$ 3.9
9,10-Dihydrophenanthrene	Phenanthrene	1	101.0 $\pm$ 3.0
9,10-Dihydroanthracene	Anthracene	1	99.7 $\pm$ 0.3
1,2,3,3a,4,5-Hexahdropyrene	Pyrene (95%)	3	90.1 $\pm$ 1.2
1-n-Decyl-3,4,5,8,9,10-Hexahdropyrene		8	60.9 $\pm$ 1.9
1,2,3,4,5,6,7,8-Octahydroanthracene	Anthracene (88%), Dihydroanthracene (8%)	4	102.0 $\pm$ 3.0
1,2,3,4-Tetrahydroquinoline	Quinoline	2	96.1 $\pm$ 3.6
Ethylbenzene		1	38.5 $\pm$ 2.0
Indan	Indene (30%), Indan (70%)	1	43.4 $\pm$ 0.6
Decalin	Tetralin, Naphthalene	5	18.5 $\pm$ 3.7
Hexadecane		8	11.9 $\pm$ 2.0
Fluorene			$\sim$ 0
o-cresol			$\sim$ 0
β -naphthol			$\sim$ 0
Acenaphthene			possible polymerization

Table 4
Hydrogen Evolution by Catalytic Dehydrogenation
of Coal Liquids

Solvent	Hydrogen Evolved (ml H ₂ /g fraction)	Weight % of Fraction			Total Hydrogen Evolved (ml H ₂ /g solvent)
	Aromatic	Polar	Aromatic	Polar	
C0	26.5		79.6		41.4 $\pm$ 4.7
C0-3	62.9		79.8		68.6 $\pm$ 7.0
C0-12	110.0		83.8		111.0 $\pm$ 6.0
C0-24	159.0		87.0		158.0 $\pm$ 3.0
C0-48	213.0		62.0		167.0 $\pm$ 6.0
R0-1	46.8	79.7	54.6	34.8	72.0
R0-3	80.3	71.9	49.6	40.9	82.2
Tetralin					295.0 $\pm$ 19.0 (339) ^b
Synthetic Solvent					152.0 $\pm$ 12.0 (146)

^aThe donable hydrogen is assumed to be totally in the aromatic fraction of the creosote oil series.

^bValues in parentheses indicate theoretical values.

Table 5
Comparison of Aromaticities Derived from ^{13}CMR
and the Brown-Ladner Equation

Sample	(C/H) atomic	CMR Derived Aromaticity	B-L Derived Aromaticity	Difference
<u>Whole Oil</u>				
C0	1.213	0.897	0.901	-0.004
C0-3	1.086	0.813	0.814	-0.001
C0-12	0.945	0.614	0.699	-0.085
C0-24	0.874	0.688	0.632	0.056
C0-48	0.733	0.371	0.423	-0.052
R0-1	0.883	0.614	0.641	-0.027
R0-3	0.794	0.538	0.533	-0.005
Mobil Synthetic Solvent	0.917	0.735	0.726	0.009

Table 6
Comparison of Transferable Hydrogen in Coal-Derived Solvents
Determined by Cyclic Alpha and Cyclic Beta Hydrogen

	Calculation Based Upon		
	Whole Oil	Aromatic Fraction	Polar Fraction
C0	0.38	0.29	
C0-3	0.73	0.53	
C0-12	1.36	1.03	
C0-24	1.63	1.24	
C0-48	2.23	1.38	
R0-1	0.89	0.43	0.35
R0-3	1.20	0.73	0.51

Table 7
Transferable Hydrogen in Coal-Derived Liquids

Solvent	22-31 ppm	22.5-37.0	¹ H NMR	Combined ¹³ CMR - ¹ H NMR	Catalytic Dehydrogenation
C0	0.23	0.45	0.29	0.22-0.26	0.19 $\pm$ 0.02
C0-3	0.33	0.44	0.53	0.50-0.58	0.45 $\pm$ 0.08
C0-12	0.82	0.94	1.03	1.49-1.75	0.83 $\pm$ 0.07
C0-24	1.31	1.61	1.24	2.03-2.38	1.24 $\pm$ 0.03
C0-48	1.26	1.75	1.38	1.50-1.75	1.19 $\pm$ 0.01
RU-1	0.63	0.96	0.78	0.22-0.26	0.48
RO-3	0.87	1.33	1.24	0.98-1.16	0.62
Synthetic* Solvent	1.30	1.25	1.45	1.12-1.31	1.37 $\pm$ 0.11

*The theoretical value for the synthetic solvent is 1.27.

Figure Captions

- Figure 1. Gas Buret Used for Measuring Hydrogen Produced by Catalytic Dehydrogenation.
- Figure 2. Evolution of Hydrogen from the Dehydrogenation of 1-Methylnaphthalene.
- Figure 3. Coal Conversion as a Function of Total Hydrogen Content;
Creosote Oils; ● Recycle Solvents; ▼ Tetralin; ▲ Decalin;
□ 1-Methylnaphthalene; ○ Synthetic Solvent.
- Figure 4. Amounts of Saturates, Aromatics and Polars Recovered by HPLC Fractionation.
- Figure 5. Parity Plot of Transferable Hydrogen, H_D , Using ^{13}CMR (22-31 ppm window) and Catalytic Solvent Dehydrogenation.
- Figure 6. Coal Dissolution as a Function of Transferable Hydrogen Determined by ^{13}CMR (22-31 ppm window). ▲ Hydrogenated Creosote Oils; ▲ Recycle Oils; ▲ Synthetic Solvent.
- Figure 7. Coal Dissolution as a Function of Transferable Hydrogen Determined by $^1\text{HNMR}$ (cyclic alpha and beta protons). □ Hydrogenated Creosote Oils; ■ Recycle Oils; □ Synthetic Solvent.
- Figure 8. Coal Dissolution as a Function of Transferable Hydrogen Determined by Catalytic Dehydrogenation. ○ Hydrogenated Creosote Oils; ● Recycle Oils; ● Synthetic Solvent.
- Figure 9. Coal Dissolution as a Function of Transferable Hydrogen Determined by Combined ^{13}CMR and $^1\text{HNMR}$. CO = Hydrogenated Creosote Oils; RO = Recycle Oils; SS = Synthetic Solvent.