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Coal Liquefaction Process Streams Characterization and Evaluation

Assessment of Hydroaromatic Content and Hydrogen Donor Ability of Coal Liquefaction Intermediates by Means of Catalytic Dehydrogenation

Topical Report

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February 1994

Under Contract to:

United States Department of Energy
Contract No. DE-AC22-89PC89883

U.S. DOE Patent Clearance was provided by
Chicago Operations Office on 1/31/94.

PROJECT ASSESSMENT

Introduction

Under subcontract from CONSOL Inc. (U.S. DOE Contract No. DE-AC22-89PC89883), The University of Pittsburgh studied the use of a catalytic dehydrogenation method for determination of the donatable hydrogen content in process-derived samples. The full report authored by the University of Pittsburgh is presented here. The following assessment briefly highlights the major findings of the project, and evaluates the potential of the method for application to coal-derived materials. These results will be incorporated by CONSOL into a general overview of the application of novel analytical techniques to coal-derived materials at the conclusion of this contract.

Summary

This study demonstrated the feasibility of using catalytic dehydrogenation for the examination of direct coal liquefaction process-derived materials. The technique, which was developed for the examination of coals, was applied to the 850 °F distillation resid of process stream samples and the tetrahydrofuran (THF)-soluble portion of those resids. Additionally, selected resid samples were silylated to block phenolic -OH groups, then subjected to the catalytic removal of hydroaromatic hydrogen to determine the effect of phenolics on hydrogen evolution and hydrogen transfer ability of the resids. The results of this study indicate that the dehydrogenation method may, with additional development, become a useful tool for the analysis of the process-derived materials.

Program Description

This report describes the work performed at the University of Pittsburgh under a subcontract from CONSOL Inc., Research and Development. CONSOL's prime contract to the U.S. Department of Energy (Contract No. DE-AC22-89PC89883, "Coal Liquefaction Process Streams Characterization and Evaluation") established a program for the analysis of direct coal liquefaction derived materials. The program involves a number of participating organizations whose analytical expertise is being applied to these materials. The broad objective of this Participants Program is to improve our understanding of fundamental coal liquefaction chemistry to

facilitate process improvement and new process development. The specific approach to achieving this objective is to provide a bridge between direct coal liquefaction process development and analytical chemistry by demonstrating the application of various advanced analytical methods to coal liquefaction materials. The methodologies (or techniques) of interest are those which are novel in their application for the support of coal liquefaction and those which have not been fully demonstrated in this application. CONSOL is providing well-documented samples from different direct coal liquefaction production facilities to the program participants. The participants are required to interpret their analytical data in context to the processing conditions under which the samples were generated. The methodology employed is then evaluated for its usefulness in analyzing direct coal liquefaction derived materials.

Participant's Methodology

The University of Pittsburgh used a catalytic dehydrogenation technique for the examination of four 850 °F⁺ distillation resids of process stream samples and the corresponding tetrahydrofuran (THF)-soluble portion of those four resids. The experimental procedures used for the catalytic dehydrogenation of the resids and the analytical work-up of the dehydrogenated products is described on pages 6 through 10 of the attached report. In addition, one ash-containing resid and the corresponding deashed resid were silylated to block the phenolic -OH groups, then catalytically dehydrogenated. The procedure for silylation is described on page 9 of the attached report. The samples were obtained originally from the recycle streams of the Wilsonville pilot plant and the HRI Inc. bench unit. Pairs of samples with and without ash and insoluble organic material (IOM) were provided for study of the effects of ash and IOM on the catalytic dehydrogenation results.

Participant's Major Findings

The following principal observations for the application of catalytic dehydrogenation to coal liquefaction resids were reported by the University of Pittsburgh. An expanded discussion can be found in the attached report, pages 10 through 19.

Two quantities were defined and then measured by the researchers at Pitt. The first quantity, total donatable hydrogen content is defined as the cumulative amount of hydrogen evolved from the resid samples at 150 min in a phenanthridine vehicle at 350 °C with Pd/CaCO₃ as catalyst. It represents all hydrogen that can be evolved, under these conditions, from the hydroaromatic compounds and, as was demonstrated in this study, phenolic -OH groups in the samples. The rate of H₂ evolution also was monitored. The second quantity, hydrogen donor ability, is defined as the cumulative amount of hydrogen transferred to a hydrogen acceptor (stilbene) at 300 min at a lower temperature (248 °C) in quinaldine with Pd/C catalyst. The amount of hydrogen transferred to the stilbene was determined by monitoring the accumulation of bibenzyl in the reaction system by GC/MS. This quantity is expected to represent that amount of hydrogen that is reactive under these conditions with a "coal-like" acceptor. A series of experiments were performed to establish these reaction conditions as optimum for work with direct coal liquefaction resids. (See pages 10 through 14 in the attached report).

The rate of H₂ evolution varies for all samples studied in the reaction system with Pd/CaCO₃ as catalyst, and phenanthridine as a vehicle. The evolution rate for all samples was greatest at the beginning of the reaction and tapered off at approximately 120 min. At 150 minutes, the total amount of hydrogen evolved from the eight samples varied substantially (from 175 cc/g to 286 cc/g). The evolved hydrogen is between one-third and one-fifth of the initial hydrogen content of the samples.

Pitt compared the hydrogen donor abilities of the resid derived from an Illinois No. 6 coal (Sample 2) and of an Illinois No. 6 coal sample previously determined. The total donatable hydrogen content of the resid was about 30% higher than that of the starting coal. Pitt interprets this finding to indicate that some of the polycyclic aromatic rings of the coal were hydrogenated to produce the resid in the direct coal liquefaction process. The aromaticities of the samples were determined before (by CONSOL) and after dehydrogenation (by Pitt) using ¹H-NMR. The aromatic proton content of the resids increased in each case indicating that hydroaromatic hydrogen was removed in the catalytic hydrogenation procedure.

The hydrogen donor ability of the eight samples was determined, as defined above. On an absolute basis, the resids were found to donate 5 to 10% of their total hydrogen content to the acceptor. The samples have the following order of donor ability: Ref. 2 > Ref. 4 > Ref. 8 > Ref. 3 > Ref. 1 > Ref. 6 > Ref. 5 > Ref. 7. Samples 2, 4, and 6 are THF-soluble portions of Samples 1, 3, and 5. It was found that on an absolute basis the hydrogen donor ability of the ash- and IOM-containing samples is lower than that of the ash-free samples. Two explanations offered by Pitt are 1. that the mineral matter ties up the donatable hydrogen or 2. the mineral matter interferes with the effectiveness of the Pd catalyst. Recalculation of the data on an MAF basis (CONSOL Table A) shows that the absolute differences noted by Pitt are small (e.g., for samples 3 and 4, the difference is less than 5%). This indicates that the ash is a diluent and does not affect the hydrogen evolution.

Blocking the phenolic hydrogen by silylation reduced the amount of total donatable hydrogen, relative to the initial sample (on an absolute basis). The difference in hydrogen evolution between the initial sample and the silylated sample was apparent only after 60 min of reaction. Pitt interprets this to mean that the hydrogen in the phenolic groups is released after the hydroaromatic hydrogen is removed, and thus that the phenolics are poorer hydrogen donors than the hydroaromatics.

CONSOL Evaluation

In this study, the catalytic dehydrogenation technique was explored for use with direct coal liquefaction-derived materials. The researchers at the University of Pittsburgh were able to draw some conclusions on the relative ease of hydrogen donation and hydrogen donor ability of the resids studied. All evaluation was done by Pitt on values presented on an absolute basis (i.e., cc H₂ per gram of sample).

Recasting those values on a gram hydrogen evolved or reacted with stilbene per gram hydrogen in the sample basis was done using CONSOL elemental analytical data and Pitt's catalytic dehydrogenation data (CONSOL Table A). Many of Pitt's conclusions are supported in this presentation of the data. It is apparent that the presence of ash and IOM in the resid reduces the total donatable hydrogen for all three sets

of samples (1 and 2, 3 and 4, and 5 and 6). However, on this basis, the hydrogen donor ability is barely affected by the ash and IOM content. Also, the two HRI samples can be seen to be very different from each other. The sample produced from HRI Run CC-15, in a period of the run when the feed coal was impregnated with an iron catalyst, has a much higher donatable hydrogen content and hydrogen donor ability than a sample produced in a different run at HRI from the same feed coal (Sample 7). Finally, as was pointed out by Pitt, the HRI CC-15 PFL (Sample 8) is seen to have a much higher hydrogen donor ability and donatable hydrogen content than the resid produced from the same feed coal at the Wilsonville facility (Samples 5 and 6).

The data presented on a percent of hydrogen in the resid basis indicate that the resids produced from the Pittsburgh seam coal have a higher hydrogen donor ability and donatable hydrogen content (as a percent of total hydrogen) than the Illinois No. 6 coal-derived resids. This is reverse of the order obtained by evaluating the data on an absolute basis.

The catalytic dehydrogenation data produced in this project suggest that this method can be used to determine the amount of donatable hydrogen in the resids. Differences among samples were distinguishable and they appear to relate to factors such as coal rank, processing facility, and ash content.

The brief investigation of the effect of phenolic -OH on the total donatable hydrogen content indicates that silylation of the phenolic -OH prior to catalytic dehydrogenation reduces by a small amount the total donatable hydrogen (about 10%). When the data are examined on the basis of grams of hydrogen evolved per gram of hydrogen in the sample as phenolic -OH, the reduced amount of evolved hydrogen is more than twice the amount of the phenolic -OH present in the sample. This indicates that the silylation technique may not be optimum for reaction with the resids. However, if it can be assumed that all of the phenolic -OH are silylated, this technique may be useful for investigating the effect of phenolic -OH on catalytic dehydrogenation.

The equipment used in these studies was designed and built at the University of Pittsburgh. It is not commercially available equipment. The time required to perform a single experiment is approximately one day.

Further Development

A catalytic dehydrogenation method for the analysis of direct coal liquefaction resid samples was explored in this project. A number of avenues for further research are suggested by the findings presented here. They are the following: 1) Improved phenolic -OH derivatization techniques, and studies with samples of different phenolic -OH content are recommended to determine the effect of phenolic -OH on the dehydrogenation of the resids which in turn impacts on the mechanism and kinetics of coal liquefaction. 2) A better understanding of the influence of the ash and insoluble organics on the determined hydrogen donor ability and donatable hydrogen content is desirable. 3) Batch microreactor studies using a suite of partially dehydrogenated resids and standard coal could provide information for kinetic and mechanistic modeling. 4) The researchers at Pitt suggest that batch microreactor studies using resids and dehydrogenation catalysts could evaluate catalyst reactivity. 5) Pitt also recommends the use of solid-state NMR spectrometry for analysis of the dehydrogenated resids.

Participant's Statement of Work

Optimum catalytic dehydrogenation conditions will be determined with two tetrahydrofuran (THF)-soluble 850 °F⁺ distillation resid samples (Reference Nos. 5 and 7). This will be accomplished by varying the solvent, by addition of hydrogen acceptor, and by examining the dehydrogenated resid at different times by NMR. Based on this optimization study, resid samples with Reference Nos. 3, 4, 6 and 8 will be catalytically dehydrogenated. These samples will be monitored for hydrogen evolution and the partially or completely dehydrogenated resid samples will be removed from the reaction flask at various times and examined by NMR. All six samples will be evaluated for the amount of hydroaromatic hydrogen. The hydrogen donor ability of the resids will be determined and compared. The effect of mineral matter on the efficacy of hydrogen donatability will be determined. If time permits, samples

with Reference Nos. 1 and 2 will be studied in the same way. The phenolic -OH groups in two samples will be derivatized to trimethylsilyl ethers. These samples then will be catalytically dehydrogenated to determine the effect of phenolics on hydrogen evolution and the hydrogen transfer ability of the resids.

The samples will be supplied to the University of Pittsburgh with the following information, as available: elemental analyses, ash content, ash elemental analysis, phenolic -OH concentration, calorific value, hydrogen classes by $^1\text{H-NMR}$, and the full history of the sample (plant, process conditions, age, and storage conditions). The samples are the 850 °F distillation resids of whole process oils obtained from the recycle streams in direct coal liquefaction facilities, and the THF-soluble portion of the 850 °F distillation resids. The resids contain THF-insoluble organic material and ash. Sample size will be 1-10 g, based on availability.

CONSOL TABLE A

Sample Number	Sample Description: Run, Coal, ashy or THF-soluble, wt % H, as det. basis (a)	Total Donatable H ₂ (Absolute Basis), cc H ₂ /g sample (b)	Total Donatable H ₂ (Absolute Basis) cc H ₂ /g MAF sample)	Total Donatable H ₂ as percent of Resid H ₂ Content, %	Hydrogen Donor Ability (Absolute Basis), cc H ₂ /g sample ^c	Hydrogen Donor Ability as percent of Resid H ₂ Content, %
1	Wilsonville 257, Illinois No. 6, ashy, 7.33	236	260	28.6	67.7	8.3
2	Wilsonville 257, Illinois No. 6, THF-soluble, 8.15	286	286	31.3	74.3	8.2
3	Wilsonville 259, Pittsburgh seam, ashy, 5.95	215	235	32.3	68.9	10.3
4	Wilsonville 259, Pittsburgh seam, THF-soluble, 6.74	246	246	32.5	70.0	9.3
5	Wilsonville 262 B, Wyodak and Anderson, ashy, 6.58	175	202	23.7	49.3	6.7
6	Wilsonville 262 B, Wyodak and Anderson, THF-soluble, 8.19	248	248	27.0	61.7	6.7
7	HRI CC-2, P2, Wyodak and Anderson, THF-soluble, 8.16	194		21.2	48.7	5.4
8	HRI CC-15, P9, Wyodak and Anderson, THF-soluble, 7.46	260		31.1	71.3	8.5

a) analysis provided by CONSOL

b) taken from Table 10 (see attached report)

c) taken from Table 12 (see attached report)

**ASSESSMENT OF HYDROAROMATIC CONTENT AND HYDROGEN DONOR
ABILITY OF COAL LIQUEFACTION INTERMEDIATES BY MEANS OF
CATALYTIC DEHYDROGENATION**

Final Report

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SUMMARY

Eight well-documented samples obtained from process development units were provided by CONSOL Inc. These samples are designated in the sample list (see Appendix A). The plan of this research is to determine donatable hydrogen content and hydrogen donor ability by means of catalytic dehydrogenation and to explore the possibility that catalytic dehydrogenation can be used as an analytical method for determination of the reactivity of DCL resids and to achieve insights into the chemistry of DCL. Optimum catalytic dehydrogenation conditions were determined with two distillation resids (Reference Nos. 5 and 7). This has been accomplished by varying the dehydrogenation vehicles, by addition of a hydrogen acceptor, and by examining the dehydrogenated resids at different reaction times by ^1H -NMR. Phenanthridine (b.p. 350°C) was found to be a good high boiling solvent, but quinaldine (248°C), a low boiling solvent, also was found to be effective but only in the presence of a hydrogen acceptor. Stilbene, in the presence of quinaldine, is an effective hydrogen acceptor in the catalytic dehydrogenation of the resids at low temperatures. The maximum amount of hydrogen transferred to stilbene was comparable to the amount of hydrogen evolved within 150 minutes when phenanthridine was used as a vehicle. It appeared that, within 150 minutes, the hydrogen that was evolved was hydroaromatic in nature, whereas beyond 150 minutes, adduction between vehicle and resid became a chief source of hydrogen. Evidence for this was obtained by ^1H -NMR and elemental nitrogen analysis. The amount of hydrogen evolved within 150 minutes was chosen to represent total donatable hydrogen content.

Based on the optimization studies, resid samples 1,2,3,4, 6, and 8, were catalytically dehydrogenated using both the high boiling vehicle and the low boiling vehicle. The reaction

was interrupted at different time intervals to obtain partially dehydrogenated samples which were then characterized by ^1H -NMR. It was found that in time their aromaticity increased considerably. The hydrogen donor ability of these resid samples was determined based on hydrogen transfer ability to a hydrogen acceptor at low temperature. It appeared that samples 2,4 and 8, THF-soluble resids, should behave as good donor solvents in coal liquefaction.

The effect of phenolic groups on the evolution of hydroaromatic hydrogen was studied. The phenolic -OH groups in two samples (refs. 5 and 6) were converted to their trimethylsilyl ethers. The phenolic -OH groups did give off hydrogen at 350°C in phenanthridine. It was ascertained by GC-MS that reaction between -OH and aromatics took place and molecular hydrogen was released from the reaction. It was found that the rate of hydrogen released from -OH groups was slower than from hydroaromatic hydrogen, implying that hydroaromatic hydrogen is more readily donated than phenolic hydrogen.

BACKGROUND

Hydrogen donor and transfer reactions are of major importance in the direct liquefaction of coal (DCL). Few efforts have been directed towards developing a direct method for determination of the amount, nature and reactivity of hydroaromatic hydrogen that exists in coal. Although ^1H -NMR and ^{13}C -NMR techniques have been used for the evaluation of hydroaromatic hydrogen, and this approach is suitable for distillate fractions, but residual materials give diffuse spectra that make it difficult for quantitative analysis. Studies of the catalytic dehydrogenation of coal and recycle solvents can provide valuable information on the ease of hydrogen transfer from hydroaromatic entities and from solvents to coal.

In the 1960's, Reggel and coworkers^[1,2] studied the catalytic dehydrogenation of coal

using a 5% Pd/CaCO₃ catalyst at the boiling point of various solvents. It appeared that vehicles with low reduction potentials were more effective than vehicles of higher reduction potentials in the removal of hydrogen from coal^[3]. With this technique, they concluded that coals of about 76% carbon (maf) contain considerable hydroaromatic hydrogen with a maximum of about 33 atoms of hydrogen removed per 100 carbon atoms. Much of their work was aimed at studying coal structure and it was suggested that lignite and subbituminous coal contain substituted benzene rings with little hydroaromatic structures.

The vehicles used in most of the previous work are high boiling compounds such as phenanthridine (b.p. 350 °C)^[3,4]. The suggestion that use of a high-boiling solvent, indeed a nitrogen-containing vehicle, could lead to side reactions is valid^[5]. We found that we could use low-boiling solvents in the presence of a hydrogen acceptor to improve dehydrogenation efficiency and lower the tendency towards adduction. Experiments were then carried out with quinaldine (b.p. 248 °C) and 2-methylnaphthalene (b.p. 243 °C). Similar results were obtained with both solvents^[6]. Quinaldine and 2-methylnaphthalene are known to be good electron transfer reagents and this is probably responsible for their effectiveness.

Several hydroaromatic compounds were dehydrogenated in the presence of stilbene with quinaldine as the vehicle in an attempt to elucidate the mechanism of hydrogen transfer^[6]. The rate of the formation of intermediates was measured and the hydrogen transfer ability of following compounds was found to be in the following order:

Hexahydroanthracene > Dihydroanthracene, Dihydrophenanthrene > Tetrahydroanthracene > Octahydroanthracene. This is in keeping with the recent findings of Bate and Harrison^[7] who found the type of donor present may be more important than the total hydrogen donor content

for coal liquefaction.

Based on our findings, a mechanism for the catalytic dehydrogenation of 9,10-dihydroanthracene (9,10-DHA) was proposed to explain the reaction pathways involved in dehydrogenation with palladium as catalyst^[6]. It is assumed that, initially, an electron transfer from palladium to vehicle takes place followed by a proton transfer from the hydroaromatic compound to the reduced solvent. It is assumed that the hydrogen release is the rate controlling step:

A model equation was derived and fitted to our experimental data using a numerical analysis method. The results indicate that this model expression describes the experimental curve very well.

Coal conversion is influenced by the amount, and especially the quality, of donor solvents^[7]. It has also been suggested that catalytic dehydrogenation of hydroaromatics in coal may be a useful method to gain insight into catalysis of coal liquefaction^[8]. In the latter case, no direct evidence has been obtained to correlate catalytic dehydrogenation and performance of

those materials in coal liquefaction. As a result, we catalytically dehydrogenated 9,10-dihydroanthracene (DHA) and 9,10-dihydrophenanthrene (DHP); the rate of hydrogen removal from the two hydroaromatics was compared and related to their performance in DCL^[9]. Catalytic dehydrogenation of the mixture of 9,10-DHA and 9,10-DHP showed that 9,10-DHP tended to transfer hydrogen to a hydrogen acceptor whereas 9,10-DHA was more likely to lose molecular hydrogen to the gas phase (Figure 1). Under DCL conditions, both higher conversion and oil yield were obtained with 9,10-DHP as the donor solvent (Table 1), suggesting that a good hydrogen transfer agent is the one that can transfer hydrogen to coal at the right time and conditions.

Catalytic dehydrogenation of Illinois No.6 coal and characterization of the dehydrogenation residues by ¹H-NMR were conducted to identify structural changes in relation to DCL^[9]. As expected, the aromaticity of the coal residue increased proportionally to the amount of H₂ evolved (Table 2). It appears that removal of hydroaromatic hydrogen occurred under the conditions employed.

Results show that catalytic dehydrogenation, coupled with ¹H-NMR analysis, is a valuable analytical technique to assess the amount and the nature of hydroaromatic hydrogen in coal and recycle solvents.

Curtis et al. mentioned that compounds typically considered to function as hydrogen donors are hydroaromatics and phenols^[10]. Structural transformation between different hydroaromatics may take place during catalytic dehydrogenation of resids, suggesting the interaction between different hydroaromatic structures may exist^[6]. However, the interaction between phenolic groups and hydroaromatic structures is not clear. Catalytic dehydrogenation

of the model compound 9-phenanthrol with phenanthridine as vehicle showed that the -OH group attached to a aromatic ring tended to release hydrogen through an adduction reaction. This type of reaction only occurs at high temperatures ($>350^{\circ}\text{C}$).

Illinois No. 6 and Pittsburgh seam coals, believed to be rich in -OH groups, were silylated and then dehydrogenated as a test of the silylation method. The silylated Pittsburgh seam coals gave off 13.4 cc/g less hydrogen compared with the original coal, whereas silylated Illinois No.6 coal gives off 27.2 cc less hydrogen (Table 3). This suggests that phenolic groups may influence the dehydrogenation of hydroaromatic hydrogen.

In this report, the catalytic dehydrogenation technique was applied to the resids obtained from a DCL process. The objectives of this study are i) to determine the fate of hydroaromatic hydrogen during catalytic dehydrogenation and donor abilities of DCL resids ii) to explore the possibility that catalytic dehydrogenation can be used as an analytical method for determination of the reactivity of DCL resids and to achieve insights into the chemistry of DCL. Such data are important for process development and are difficult to acquire by any other means.

EXPERIMENTAL

Dehydrogenation Apparatus

The dehydrogenation system is designed to provide for automatic data recording. Reactions were carried out in a three-necked flask at atmospheric pressure. The palladium catalyst (5.0 wt% Pd on CaCO_3 or active carbon) was reduced with flowing hydrogen at 150°C for one hour prior to reaction. The heating rate for reduction was $5^{\circ}\text{C}/\text{min}$; the temperature was maintained at 150°C (within $\pm 1^{\circ}\text{C}$). After the flask was cooled to room temperature under hydrogen, the model compound and vehicle were charged into the flask containing a magnetic stirring bar. The

system was purged with He for 20 minutes and the flask then fitted with a heating mantle. Evolved gases from the dehydrogenation reaction were taken from the middle neck and collected over mercury in a burette. The mercury level used to maintain the atmospheric pressure was controlled by a bulb mounted on a slide mechanism, by which the mercury level in both the bulb and burette were equalized. The slide mechanism is connected to a potentiometer through a string. Five volts are imposed across the potentiometer by a voltage regulator. By connecting the potentiometer wiper and neutral lead to the interface computer, the output voltage was employed to define the position of the mercury level, providing a continuous recording of the gas volume within the burette.

Our previous studies showed that supported palladium catalysts are good catalysts for dehydrogenation, especially for hydrogen transfer in the presence of a hydrogen acceptor^[6]. At high temperatures (phenanthridine as vehicle) the surface area of the support (CaCO_3 or activated carbon) does not influence the amount of hydrogen evolved as H_2 gas. It was found that the amount of hydrogen evolved varied only slightly when the ratio of catalyst/substrate was greater than 2.0. The amount of catalyst most frequently used in this study was 0.300 gram and the amount of resid was 0.15 gram. The amount of solvent used in each run was 3.00 g. In the experiments where phenanthridine was used as vehicle, the use of Pd/CaCO_3 catalyst is preferred since it is easy to wash out CaCO_3 with HCl (aq.). The data measured in hydrogen volume was collected step-wise.

Analysis of Dehydrogenation Products

The yield of hydrogen evolved was calculated from the difference of hydrogen evolved from the dehydrogenation of the model compound and a blank run. The conditions for a blank

run were the same as the dehydrogenation run except that no resid was present in blank run. The hydrogen yield is expressed as the percentage of the theoretical available hydroaromatic hydrogen in the model compound. For example, the theoretical calculation of the hydroaromatic hydrogen in 9,10-DHA (2 atoms of hydrogen per molecule) is 140.8 cc/gram (25 °C and 740 mm of Hg). In the presence of stilbene, a hydrogen acceptor, hydroaromatic hydrogen was mostly transferred to the hydrogen acceptor rather than evolved as hydrogen gas.

For reaction products in which a hydrogen acceptor was present, the CH_2Cl_2 soluble fraction were obtained by washing of the dehydrogenation residues in 50.0 ml CH_2Cl_2 followed by vacuum filtration. The filter cake (CH_2Cl_2 insoluble dehydrogenated resid and catalyst) was discarded. The liquid filtrate is saved for GC-MS analysis. The hydrogenation product derived from stilbene is bibenzyl whose GC retention time was identified by GC-MS. The amount of hydrogen transferred was measured from the amount of bibenzyl formed.

Gas samples were removed from the sample port and analyzed by GC (Hewlett Packard 5880A). Only CH_2Cl_2 or CDCl_3 soluble dehydrogenation residues were analyzed by GC-MS and NMR. The GC used is a HP-5890 series II and the mass spectrometer is a HP-5970 series mass selective detector. The NMR instrument is a Bruker 300MHz. Organic chemicals were obtained from Aldrich Chemical Inc., catalysts were obtained from Strem Chemical Co. and from the Engelhard Corp. (Pd/ CaCO_3 , Pd/C).

^1H -NMR Analysis

Analysis of the dehydrogenated resids (CDCl_3 soluble) was carried out by ^1H -NMR. The methodology consists of removal of the basic nitrogen-containing vehicles, phenanthridine or quinaldine, by acidic solution (HCL). Since too high an acidity might dissolve constituents

within the dehydrogenated resids, an 0.5 M HCl (aq) solution was chosen to wash the dehydrogenation residue followed by filtration. The washing was stopped until no phenanthridine was detected in the filtrate as determined by NMR. The samples were then dissolved in either TDF (tetradeuterofuran) or CDCl_3 with 1% v/v TMS (tetramethylsilane) added for a reference signal. 3.5 ml of dissolved sample were placed in 10 mm NMR tubes followed by 30 minutes sonication to enhance dissolution of the solid sample (0.0100g). It is difficult to dissolve the dehydrogenated resid in NMR solvents. The NMR solvent-insoluble was filtered. The Bruker 300 MHz NMR instrument with 10 mm liquid ^1H probe was used to characterize the dehydrogenation residues. It was found that the decrease in hydroaromatic content in the specific coal resids can be monitored by the NMR spectra of the dissolved resids at various reaction times.

Integrations were performed in duplicate on the instrument; They were divided into seven regions generally corresponding to seven proton types, consistent with the assignment in CONSOL's analytical information (Appendix D).

Examination of the Phenolic Effect

Samples 5 and 6 which contain the highest amounts of -OH (Appendix B), were selected to study the effect of phenolic groups on the catalytic removal of hydroaromatic hydrogen. For the silylation procedure excess material was initially chosen (1.00 gram) allowing for multiple dehydrogenation reactions. The mass of product formed was 1.042 g, therefore 0.600 g of hexamethyldisilazane was required for complete conversion of the -OH functional groups to their silylethers. One gram samples of the resid, ground to minus 100-mesh and dried to constant weight in a vacuum oven at 90°C, were refluxed under nitrogen in a solution of few drops of

chlorotrimethylsilane and 10 ml of hexamethyldisilazane. The solution was refluxed under flow of helium for eight hours under atmospheric pressure and 125°C; excess reagents were then removed by petroleum ether. The product was dried in a vacuum oven at 90°C to constant weight.

Infrared analysis was performed to ascertain the extent of the phenolic group thus blocked. The infrared spectra were obtained using a Mattson instrument. The -OH stretch band between 3200 cm^{-1} and 3400 cm^{-1} was integrated to obtain a qualitative analysis. The resolution of the instrument is 4 cm^{-1} . Samples were analyzed as KBr pellets. Best results were obtained by hand grinding the potassium bromide with the powdered sample in an agate mortar and pestle for 10 minutes, followed by pelleting in a hydraulic press. A potassium bromide pellet was used as a reference.

RESULTS AND DISCUSSION

1. Determination of the Optimum Conditions

Samples 5 and 7 were used to determine optimum dehydrogenation conditions. A series of experiments were performed to help determine optimum reaction times, vehicles, hydrogen acceptors, and amounts of Pd catalyst.

a) Vehicles

We previously found that the rate of hydrogen removal and the final yield were dependent upon the type of vehicle employed in catalytic dehydrogenation^[6]. Two physical properties of the vehicle which have been found to affect the hydrogen evolution and hydrogen transfer of a hydroaromatic compounds are the boiling point and reduction potential.

Initially, catalytic dehydrogenation of sample 5 was conducted with phenanthridine (b.p.

350°C) and pyrene (b.p. 393°C) as vehicles. The catalyst used for the experiments was Pd/CaCO₃. Although pyrene boils at 393°C, 43°C higher than phenanthridine, the amount of molecular hydrogen removed from sample 5 at 300 minutes with pyrene as vehicle was substantially lower. About 47 cc/g more hydrogen is evolved per gram of resid with phenanthridine as a vehicle (Figure 2). The lower effectiveness of pyrene is ascribed to its higher reduction potential (-1.77 v). In catalytic dehydrogenation, the vehicle is believed to function as an electron and hydrogen transfer reagent. The use of phenanthridine, a nitrogen containing compound with lower reduction potential (-1.50 v), promotes electron transfer, believed to be a crucial step in catalytic dehydrogenation.

Catalytic dehydrogenation conducted at high temperatures is likely to result in adduction reactions between vehicle-vehicle or vehicle-resid. As a result, a low boiling and low reduction potential solvent, quinaldine (b.p. 248°C, reduction potential -1.48), was employed in the catalytic dehydrogenation of samples 5 and 7 with Pd/CaCO₃ (surface area 12 m²/g) and Pd/C (surface area 80 m²/g) as catalysts, respectively. The dehydrogenation reactions were carried out at 248°C, the boiling point of quinaldine. It can be seen from Table 4 that only about 19 cc/g of hydrogen were removed from samples 5 or 7 by Pd/CaCO₃ with quinaldine as a vehicle, whereas the use of Pd/C leads to a significant amount (142-155 cc/g) of hydrogen evolution. It seems that Pd/C exhibits higher activity towards dehydrogenation of the resids at low temperatures, probably because of its high surface area.

The presence of stilbene readily promotes the removal of hydroaromatic hydrogen from refs. 5 and 7 (Table 5). The amount of hydrogen transferred from ref. 7 to stilbene is about 50 cc/g higher than in the absence of stilbene. We have previously found that the presence of

stilbene enhanced the hydrogen transfer efficiency in palladium catalyzed dehydrogenation, since the adsorbed stilbene on Pd⁰ readily helps transfer hydrogen^[6]. Further ¹H-NMR analysis revealed that removal of hydroaromatic hydrogen likely took place with quinaldine as vehicle.

As shown in Table 6, the amount of hydrogen evolved after 300 minutes with phenanthridine as vehicle increases slowly as the dehydrogenation proceeds (4-5 cc/g.hr evolved after 300 minutes). Interestingly, the total amount of hydrogen transferred to stilbene at 300 minutes is comparable with the amount of hydrogen evolved within 150 min when phenanthridine is used as a vehicle. This suggests that, at high temperature with phenanthridine as vehicle, removal of hydroaromatic hydrogen may be predominant within 150 minutes. After 150 minutes, side reactions such as addition reactions between vehicle and resids may become a source of hydrogen evolution. This potulate is consistent with nitrogen analysis of partially dehydrogenated resids (Table 7).

It seems that both phenanthridine and quinaldine are good vehicles for catalytic dehydrogenation of the resids. However, the use of phenanthridine leads to a faster evolution of molecular hydrogen but more side reactions may occur as the reaction proceeds.

b) Catalysts and Hydrogen Acceptor

Our previous studies showed that supported palladium catalysts are good catalysts for dehydrogenation, especially for hydrogen transfer in the presence of a hydrogen acceptor^[6]. At high temperatures (phenanthridine as vehicle) the surface area of the support (CaCO₃ or activated carbon) does not influence the amount of hydrogen evolved as H₂ gas. It was found that the amount of hydrogen evolved varied only slightly when the ratio of catalyst/substrate was greater than 2.0. The amount of catalyst most frequently used in this study was 0.300 gram and the

amount of resid was 0.15 gram. In the experiments where phenanthridine was used as vehicle, the use of Pd/CaCO₃ catalyst is preferred since it is easy to wash out CaCO₃ with aq. HCl.

In experiments where quinaldine was used as a vehicle, the surface area of the support may affect the hydrogen evolution. We believe that the dehydrogenation reaction is catalyzed by the Pd^[6]. The higher surface area of the support will help the dispersion of Pd on the support therefore increasing the number of active sites.

c) Optimum Reaction Time

Catalytic dehydrogenation of samples 5 and 7 was performed five times (Runs 1-5). The analyses were performed by interrupting the reaction at different time intervals. The data are given in Tables 8 and 9. Profiles of hydrogen evolution from these two samples for Runs 3,4, and 5 of each sample are plotted in Figures 3 through 8. During the initial stage (0-15 minutes), a small amount of hydrogen evolved as molecular hydrogen. Based on our previous studies using model compounds^[6], the transformation from one hydroaromatic structure to another hydroaromatic structure probably occurred within resid at this stage.

As shown in Figures 5 and 8, a large quantity of hydrogen is evolved within the period from 15 minutes to 150 minutes; hydrogen evolution rate then decreases after 150 minutes. The nitrogen content of partially dehydrogenated resids (ref. 5) obtained at 150 minutes and 300 minutes was analyzed by Galbraith Labs., Inc. (Table 7). Nitrogen content of the starting resid (ref.5) is 1.1 wt%. It was shown that its dehydrogenated residue obtained at 150 minutes contains 2.1 wt% nitrogen whereas the residues obtained at 300 minutes contains 3.5 wt% of nitrogen. The increase in nitrogen content is attributed to adduction between vehicle and resid. All the adducted phenanthridine cannot be washed out by aq. HCl. It appears that within 150 minutes

the amount of hydrogen evolved comes mainly from removal of hydroaromatic hydrogen in the resid. Some of the hydrogen evolved after 150 minutes may be due to adduction reactions.

Adduction reactions can be minimized by using a low boiling solvent, quinaldine^[6]. For most resids, the maximum amount of hydrogen transferred to stilbene (quinaldine as vehicle) is comparable to the amount of hydrogen evolved at reaction times extending up to 150 minutes with phenanthridine used as a vehicle (Table 5, 8, and 9; Figures 4-9).

To summarize, the following conclusions concerning optimum reaction conditions were obtained:

- Catalytic dehydrogenation at high temperature using phenanthridine as a vehicle, Pd/CaCO₃ as a catalyst and the reaction interrupted at 150 minutes: The amount of molecular hydrogen collected within this period is a measure of the total donatable hydrogen content.
- Catalytic dehydrogenation at low temperatures using quinaldine as a vehicle, Pd/C as catalyst in the presence of the hydrogen acceptor, stilbene. On the basis of our previous results^[6], the amount of hydrogen transferred to stilbene may depend on the structure of the hydroaromatics present in the resid and we have assumed that it represents the hydrogen donor ability of the coal the resid.

2. Determination of Donatable Hydrogen Content

On the basis of optimization studies, samples with reference Nos. 1, 2, 3, 4, 6, and 8 were catalytically dehydrogenated using Pd/CaCO₃ and phenanthridine as catalyst. The amount of H₂ evolved within 150 minutes was carefully measured and defined to be donatable hydrogen content. As shown in Figures 9 to 14 and Table 10, the rate of hydrogen evolution of these samples is quite similar. After 150 minutes, the hydrogen yield of these resids varied from 175.0

cc/g (ref.5) to 286.0 cc/g (ref.2). Compared to the total hydrogen content of the original resids, around 1/4 of total hydrogen in the resids can become a hydrogen source in DCL. The resid with reference No. of 2 was derived from Illinois No. 6 coal. Compared to the original coal, the donatable hydrogen content increased from 210 cc/g (Table 2) to 286 cc/g (Table 7), indicating that hydrogenation of polycyclic aromatics occurred during the DCL process. It appears that the donatable hydrogen contents of these resids are in the following order: ref. 2>ref. 8>ref.6, ref.4, ref.1>ref.3>ref.7>ref.5. Table 11 compares the changes of aromaticity of these samples after catalytic dehydrogenation. A considerable increase of aromaticity demonstrates that hydroaromatic hydrogen was removed. Generally, a high donatable hydrogen content means the material has the potential to function as a good hydrogen donor. However, it is difficult to postulate the hydrogen donor ability of these samples based on hydroaromatic content, because, in some cases, the hydroaromatic hydrogen content may not be consistent with their hydrogen donor ability, or efficiency of DCL performance^[6,7].

3. Determination of Hydrogen Donor Ability

Based on the comparison of hydrogen donor ability of model compounds under DCL conditions as summarized in the "Background" of this report (Table 1), the hydrogen donor ability of these resids was compared by catalytic dehydrogenation using quinaldine as a vehicle in the presence of a hydrogen acceptor. As shown in Table 12, the total amounts of hydrogen removed from samples 5 and 7 exceed that obtained from the others, but the amount of hydrogen transferred to a hydrogen acceptor is less, indicating that these two samples may not be effective in hydrogen utilization for DCL. In other words, if refs. 5 and 7 are used in DCL, they may tend to release more hydrogen to the gas phase instead of transferring it to coal. It is noteworthy that

the amount of hydrogen transferred from samples 2 and 4 to the hydrogen acceptor (stilbene) is significantly higher although the total amount of hydrogen removed from them is less. This is probably because samples 2 and 4 have higher contents of hydroaromatics. The ^1H -NMR analysis shows considerable increase in aromatic content in agreement with the amount of hydrogen transferred. The fraction of hydrogen transferred to stilbene from samples 2 and 4 exceeds 50 wt% of total hydrogen removed, implying that they are good hydrogen donors. It is reasonable to predict that the hydrogen donating efficiencies of samples 2 and 4 are better than the other resids. As far as DCL performance is concerned, we predict that samples 2,4 and 8 will be good donor solvents. On the basis of absolute amount of hydrogen transferred to stilbene (cc/g), the DCL performance (donor ability) of these resids is expected in the following order : ref.2 >ref.4>ref.8>ref.3>ref.1>ref.6>ref.5>ref.7. The (donatable) hydrogen content of the resids determined by releasing molecular hydrogen accounts for their abilities in donating hydrogen characterized by measuring the amount of hydrogen transferred to an hydrogen acceptor. But it is not pertinent to conclude that the higher the (donatable) hydrogen content the higher the hydrogen donor ability, since in some cases the two properties are not identical^[7].

4. Effect of Phenolic Group on Catalytic Removal of Hydroaromatic Hydrogen

Samples with references Nos. 5 and 6, which are rich in -OH groups based on FT-IR analysis, were chosen to study the effect of phenolic structures on catalytic removal of hydroaromatic hydrogen. The phenolic groups were blocked by forming trimethylsilyl ethers. FT-IR analysis in this laboratory shows a significant decrease in peak intensity at 3300 cm^{-1} , ascribed to the -OH binding vibration; a huge peak at 1000 cm^{-1} , ascribed to Si-O stretching vibration, appears on blocking the phenolic groups (Figures 15 and 16).

The silylated reference 6 was catalytically dehydrogenated and the hydrogen evolution rate was compared with the sample before the -OH group was blocked. As shown in Figure 17, two curves of hydrogen evolution almost overlap for 60 minutes. The difference appears gradually after 60 minutes. The difference is explained by the silylation of the phenolic groups in the resid. The difference in the amount of hydrogen (20.6 cc) released from silylated sample and unsilylated sample in Figure 17 represents the concentration of phenolic hydrogen in the resid.

Sample reference No. 5 was silylated using the same method; the silylated ref.5 gave off about 21.0 cc/gram less hydrogen as compared to the original sample (Figure 18). The difference in rate of hydrogen evolution appears after 60 minutes, implying that hydrogen in phenolic groups is released after hydroaromatic hydrogen is removed. As far as hydrogen donor ability is concerned, we expected that hydroaromatic hydrogens are better hydrogen donors than phenolic hydrogen.

5. Effect of Mineral Matter on the Hydrogen Donor Ability

Samples 2,4 and 6 are THF-soluble portion of their corresponding samples 1,3 and 5 which are ash-containing resid composite. In principle, the amount of donatable hydrogen should be the same in high and low ash resids. However, the amount of hydrogen evolved with high ash resids was lower than with ash-free resids (Table 13). Two possible explanation may exist: the mineral matter ties up donatable hydrogen or the experimental determination of donatable hydrogen is affected by the presence of mineral matter, perhaps by interacting with the palladium catalyst.

6. Catalytic Dehydrogenation in Relation to Coal Liquefaction

Reggel et al. catalytically dehydrogenated different ranks of coal⁽¹⁾. They found that the amount of hydroaromatic hydrogen evolved decreased with the increase in coal rank. However,

the hydroaromatic hydrogen evolved from subbituminous coals do not fall on the curve derived from the higher rank coals. It is possible to compare catalytic dehydrogenation results from different bituminous coals and relate them to liquefaction processes. But the results from catalytic dehydrogenation of bituminous coals should not be compared with those obtained with subbituminous coals, which contain large amount of oxygen. Fortunately, the resid received was derived from a single subbituminous coal: Black Thunder recycle oils from Wilsonville and from HRI. Since these resids are derived from the same coal, they can be compared with each DCL process but not with resids derived from the two bituminous coals.

Two bituminous and one subbituminous coals were used to produce the resids. As summarized in Appendix A, samples 1 and 2 were produced from Illinois #6 coal; samples 3 and 4 were produced from a Pittsburgh seam coal. Samples 5, 6, 7, and 8 were produced from Wyodak and Anderson seam Black Thunder coal. Samples with numbers 1 to 6 were produced from the Wilsonville whereas samples 7 and 8 were produced from HRI liquefaction systems.

Results shown in Tables 10 and 12 indicate that both donatable hydrogen content and hydrogen donor ability of sample 2 (produced from Illinois #6 coal) are greater than sample 4 (produced from Pittsburgh seam). It seems that resids produced from Illinois #6 coal are better than those produced from Pittsburgh seam coal in terms of hydrogen donor ability and probably would be better recycle solvents.

Samples 7 and 8 were produced from the same coal (Black Thunder) under different processing conditions in HRI. As summarized in Tables 10 and 12, both donatable hydrogen

content and hydrogen donor ability of sample 8 (produced from run cc-15-9ABC) are higher than that of sample 7 (produced from run cc-2-14), probably because the predispersed hydrated iron oxide catalyst employed in producing sample 8 (prepared for the test by PETC) promotes the conversion of Wyodak and Anderson seam Black Thunder coal. It appears that the pretreatment procedure employed in run cc-15-9ABC (HRI system) is a way of obtaining good quality recycle solvents.

Black Thunder coal was used as a coal in both Wilsonville and HRI coal liquefaction systems. Samples 8 (HRI) and 6 (Wilsonville) can be compared. As indicated in Tables 10 and 12, sample 8 contains a more donatable hydrogen content and is a better hydrogen donor than sample 6. It appears that sample 8 produced from the HRI liquefaction process would be a better recycle oil than sample 6 produced from the Wilsonville coal liquefaction system. Sample 7 produced from HRI contains lower donatable hydrogen content compared with samples 6 and 8 probable due to the liquefaction process.

ASSESSMENT AND SUGGESTION ON ACCOMPLISHMENT

The results reported here are interesting and important in achieving insight into the chemistry of coal liquefaction. This study demonstrates that catalytic dehydrogenation is a useful technique in determination of donatable hydrogen content and hydrogen donor ability of DCL resids. It seems probable to relate the hydrogen transfer ability of the resids to their performance in coal liquefaction. Further work could involve the following:

DCL experiments will be performed in a microreactor using these resids as donor solvents. These resids may be catalytically dehydrogenated using coal liquefaction catalysts such as MoS_2 or $\text{Fe}_2\text{O}_3/\text{SO}_4$ to compare their reactivities as dehydrogenation catalysts.

It is hard to dissolve the dehydrogenated resid in NMR solvents, making NMR characterization difficult. Solid state ^{13}C -NMR should be employed to characterize the partially dehydrogenated residues and to investigate structural transformation that may have occurred during catalytic dehydrogenation. Light DCL products may be more easily analyzed by the catalytic dehydrogenation combined with NMR analysis.

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Table 1. Effect of Donor Solvents on Liquefaction of Illinois No. 6 Coal (reference 9)

Donor solvent	Total Conversion of Coal	Oil yield	Donor solvent converted to aromatics (wt%)
9,10-dihydrophenanthrene	77.6	23.7	66.0
9,10-dihydroanthracene	70.2	21.2	84.6

Reaction conditions: 400°C, 1000 psig of He, Solvent/Coal=2:1, 60 minutes in a microreactor.

Table 2. Characterization of Residues from Catalytic Dehydrogenation of Illinois No. 6 Coal (reference 9)

Run Time(min)	Aromatic/Hydroaromatic Hydrogen by ¹ H-NMR	Amount of Hydrogen evolved(ml/g)*
60	42.9	112.5
120	68.6	161.5
180	88.9	212.0
210	96.1	227.5

Reaction conditions: Pd/CaCO₃ as catalyst, phenanthridine as solvent, H₂ measured at 25°C, 744 mmHg.

Table 3. Effect of Phenolic Groups on Catalytic Dehydrogenation of Illinois No. 6 and Pittsburgh Seam Coal

Time (min)	H ₂ evolved from Illinois No. 6 (cc/g)		H ₂ evolved from Pittsburgh Seam Coal (cc/g)	
	-OH-unblocked	-OH-blocked	-OH-unblocked	-OH blocked
0	0.0	0.0	0.0	0.0
10	35.0	42.0	34.5	33.2
20	67.5	68.0	71.2	67.5
30	75.0	80.0	106.7	96.2
60	160.2	165.5	128.0	112.6
90	190.5	190	145.9	130.7
120	225.5	210.0	163.7	151.6
150	252.2	225.0	175.5	162.1

Table 4. Catalytic Dehydrogenation of Resids at 248°C with Quinaldine as Vehicle.
Measurement obtained at 300 minutes.

Catalyst	H ₂ evolved from sample 5 (cc/g)	H ₂ evolved from sample 7 (cc/g)
Pd/CaCO ₃ (12 m ² /g)	19.4	19.0
Pd/active carbon (80 m ² /g)	142.0	154.1

Volume of H₂ measured at 23°C, 744 mm Hg.

Table 5. Effect of Hydrogen Acceptor on Removal of Hydroaromatic Hydrogen

Sample	H-removed in the presence of stilbene (cc/g)	H-removed in the absence of stilbene (cc/g)
Ref.5	190.4	142.0
Ref.7	209.2	154.1

Reaction conditions: Pd/C as catalyst, quinaldine as vehicle, 300 min reaction time. Volume of hydrogen measured at 23°C, 744 mm Hg.

Table 6. Catalytic Dehydrogenation of Ref.7 with Phenanthridine as Vehicles (Pd/CaCO₃ as catalyst, 350°C)

Vehicle	Amount of hydrogen removed (cc/g)		
	150 minutes	300 minutes	450 minutes
Quinaldine (presence of stilbene)	155.0	209.2	211.4
Phenanthridine	194.0	266.8	278.2

Table 7. Nitrogen Analysis of Dehydrogenated Resid (ref. 5)

Time	Elemental Hydrogen Content (wt %)
0	0.96
150	2.1
300	3.5

Table 8. Hydrogen Evolution from Catalytic Dehydrogenation of Ref.5 with Phenanthridine as Vehicle and Pd/CaCO₃ as Catalyst at 350°C.

Time	Run 1	Run 2	Run 3	Run 4	Run 5
0	0	0	0	0	0
5	18.1	18.0	20.5	18.8	18.7
10	26.5	24.1	23.9	24.2	22.0
15	34.21	36.7	33.1	34.5	33.2
20		42.5	40.7	46.1	44.4
30		58.2	54.2	50.8	56.6
60			87.7	88.8	84.2
90			113.5	129.4	127.8
120				141.4	147.4
150				161.4	175.0
180					217.4
240					240.7
300					260.0
Final*	34.7	50.92	140	197.0	284

* Final volume was measured after the system was cooled to room temperature.

Table 9. Hydrogen Evolution from Catalytic Dehydrogenation of Ref. 7 with Phenanthridine as Vehicle and Pd/CaCO₃ as Catalyst at 350°C

Time	Run 1	Run 2	Run 3	Run 4	Run 5
0	0	0	0	0	0
5	22.0	21.6	21.80	20.40	21.20
10	24.01	23.81	22.97	24.88	22.1
15	36.11	34.21	33.5	36.2	35.5
20		40.8	44.1	42.2	41.1
30		63.36	64.2	59.2	58.1
60			104.9	106.1	94.4
90			147.18	147.18	134.0
120				177.54	176.2
150				194.04	194.0
180					208.6
240					241.6
300					266.8
Final	39.6	61.8	161.6	220.11	290.8

Table 10. Donatable Hydrogen Content Measured by Catalytic Dehydrogenation with Phenanthridine as Vehicle

Time (Min)	H ₂ Evolved (cc/gram)							
	Ref. 1	Ref. 2	Ref. 3	Ref. 4	Ref. 5	Ref. 6	Ref. 7	Ref. 8
0	0	0	0	0	0	0	0	0
10	33.4	34.4	31.1	29.0	24.2	28.4	24.9	28.1
20	68.2	64.74	46.07	40.02	46.1	42.0	42.4	40.5
30	92.4	104.0	71.3	77.9	50.8	87.12	63.4	67.8
60	140.58	158.5	132.74	133.7	88.8	134	106.0	131.99
90	195.35	207.3	166.32	180.1	129.4	188.1	147.2	179.6
120	213.4	239.0	191.4	213.4	147.4	223.4	177.5	233.6
150	236.1	286.0	215.4	245.5	175.0	248.0	194.0	260.0

Table 11. Aromaticity of Various Samples Provided

Samples	Aromaticity	
	Initial samples ¹	150 min
1	19.9	71.0
2	21.1	62.8
3	31.5	59.1
4	31.5	70.6
5	22.6	67.8
6	21.5	53.8
7	23.4	50.1
8	14.3	66.5

1. Analyses on pyridine-soluble basis (provided by CONSOL Inc.).

Table 12. Comparison of Hydrogen Donor Abilities of Recycle Solvents with Quinaldine as Vehicle in the Presence of Stilbene.

Sample ^a	Hydroaromatic H by ¹ H NMR ^b (wt%)	Total H removed (cc/gram)	H-transferred to stilbene (cc/gram)	H ₂ evolved as H ₂ (cc/gram)	% hydrogen transferred to stilbene
1	22.2	191.1	67.7	123.4	35.4
2	22.3	119.6	74.3	45.3	62.1
3	24.3	138.2	68.9	69.3	49.9
4	24.3	139.3	70.0	69.3	50.2
5	21.6	190.6	49.3	141.3	25.9
6	22.4	159.0	61.7	97.3	38.8
7	19.7	200.7	48.7	152.0	24.3
8	18.4	174.0	71.3	102.7	41.0

a. Samples are the distillation resids from DCL furnished by CONSOL Inc.

The volume of hydrogen was measured at 25 °C, 740 mm Hg.

b. Cited from NMR data provided by CONSOL Inc.

Table 13. Effect of Mineral Matter on the Measurement of Donatable Hydrogen Content and Hydrogen Donor Ability*

Sample	Donatable Hydrogen content (cc/g) ^a	Amount of H transferred to H-acceptor (Hydrogen donor ability) ^b
1	260.3	74.6
2	286.0	74.3
3	235.4	75.3
4	245.5	70.0
5	202.1	56.9
6	248.0	61.7

* The mineral matters in samples 1, 3 and 5 were factored out.

a. Measured at 350°C with phenanthridine as a vehicle.

b. Measured at 248°C with quinaldine as a vehicle, stilbene as a hydrogen acceptor.

Catalytic dehydrogenation of the mixture of 9,10-DHA and 9,10-DHP in presence of half equivalent of hydrogen acceptor, stilbene, with Pd/C as catalyst, quinaldine as vehicle.

Figure 1

Catalytic dehydrogenation of sample 5 (ref.5) with different vehicles, Pd/CaCO₃ as catalyst.

Figure 2

Catalytic dehydrogenation of sample 5 with phenanthridine as vehicle, Pd/CaCO₃ as catalyst.

Figure 3

Catalytic dehydrogenation of sample 5 with phenanthridine as vehicle,
Pd/CaCO₃ as catalyst.

Figure 4

Catalytic dehydrogenation of sample 5 with phenanthridine as vehicle,
Pd/CaCO₃ as catalyst.

Figure 5

Catalytic dehydrogenation of sample 7 with phenanthridine as vehicle, Pd/CaCO₃ as catalyst.

Figure 6

Catalytic dehydrogenation of sample 7 with phenanthridine as vehicle, Pd/CaCO₃ as catalyst.

Figure 7

Catalytic dehydrogenation of sample 7 with phenanthridine as vehicle,
Pd/CaCO₃ as catalyst.

Figure 8

Catalytic dehydrogenation of sample 1 with phenanthridine as vehicle, Pd/CaCO₃ as catalyst.

Figure 9

Catalytic dehydrogenation of sample 2 with phenanthridine as vehicle,
Pd/CaCO₃ as catalyst.

Figure 10

Catalytic dehydrogenation of sample 3 with phenanthridine as vehicle,
Pd/CaCO₃ as catalyst.

Figure 11

Catalytic dehydrogenation of sample 4 with phenanthridine as vehicle, Pd/CaCO₃ as catalyst.

Figure 12

Catalytic dehydrogenation of sample 6 with phenanthridine as vehicle,
Pd/CaCO₃ as catalyst.

Figure 13

Catalytic dehydrogenation of sample 8 with phenanthridine as vehicle,
Pd/CaCO₃ as catalyst.

Figure 14

IR spectra of sample 5 (-OH groups are not blocked).

Figure 15

IR spectra of -OH-blocked sample 5.

Figure 16

Effect of phenolic groups on catalytic dehydrogenation of sample 6. Phenanthridine was used as vehicle, Pd/CaCO₃ as catalyst

Figure 17

Effect of phenolic groups on catalytic dehydrogenation of sample 5. Phenanthridine was used as vehicle, Pd/CaCO₃ as catalyst

Figure 18

Appendix A

Description of the Resids

Ref. No.	Seam	Mine	Source	Designation	Comments
1	Ill# 6	Burning Star 2	W; Run 257	V-131B	Resid Composite
2	Ill# 6	Burning Star 2	W; Run 257	V-131B	THF-Soluble Resid
3	Pittsburgh	Ireland	W; Run 259	V-131B	Resid Composite
4	Pittsburgh	Ireland	W; Run 259	V-131B	THF-Soluble Resid Composite
5	Wyodak and Anderson	Black Thunder	W; Run 262B	V-131B	Resid
6	Wyodak and Anderson	Black Thunder	W; Run 262B	V-131B	THF-Soluble Resid
7	Wyodak and Anderson	Black Thunder	H;Run CC-2-14	PFL	THF-Soluble Resid
8	Wyodak and Anderson	Black Thunder	H;Run CC-15-9ABC	PFL	THF-Soluble Resid

Note: W=Wilsonville; H=HRI; all Wilsonville samples are from vessel V-131B (recycle stream); all HRI samples are pressure filter liquids (PFL).

Appendix B

Phenolic -OH Group Concentration and Oxygen Content of the Resids¹

Ref. #	Seam and comments	Run	Phenolic content* OH meq/gram	Oxygen content wt % (by diff)
1	Illinois #6	W;257	0.50	1.7
2	Illinois #6 THF soluble	W;257	0.50	2.3
3	Pittsburgh	W;259	0.69	0.2
4	Pittsburgh THF soluble	W;259	0.69	1.4
5	Wyodak & Anderson	W;262B	0.73	0.18
6	Wyodak & Anderson THF soluble	W;262B	0.73	1.85
7	Wyodak & Anderson THF soluble	H;CC-2-14	0.24	1.47
8	Wyodak & Anderson THF soluble	H;CC-15- 9ABC	0.38	0.38

1. Analysis provided by CONSOL Inc.

* Note: Analysis performed THF-soluble portion of sample

Appendix C

^1H -NMR spectra of dehydrogenated sample 1 after 150 minutes

^1H -NMR spectra of dehydrogenated sample 2 after 150 minutes

^1H -NMR spectra of dehydrogenated sample 3 after 150 minutes

^1H -NMR spectra of dehydrogenated sample 5 after 150 minutes

^1H -NMR spectra of dehydrogenated sample 6 after 150 minutes

^1H -NMR spectra of dehydrogenated sample 7 after 150 minutes

^1H -NMR spectra of dehydrogenated sample 8 after 150 minutes

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Appendix D

Assignment of Proton Types *

Chem Shift (TMS), ppm	Proton Type	Description
10.5-7.15	Cond. Aromatics	Proton attached to a condensed aromatic ring
7.25-4.7	Uncond. Aromatics	Proton attached to an uncondensed aromatic ring
4.7-2.5	Cyclic Alpha	Proton on naphthenic carbon adjacent to fused aromatic ring of naphtheno-aromatic
2.5-2.0	Alkyl Alpha	Methyl or non-cyclic methylene or methyldene proton adjacent to aromatic ring
2.0-1.4	Cyclic Beta	Naphthenic protons. Naphthenic protons two positions from the aromatic ring of naphtheno-aromatics
1.4-1.0	Alkyl Beta	Interior protons of paraffins. Methyl proton two position from an aromatic ring. Non-cyclic methylene protons two or more positions from an aromatic ring
1.0-0.5	Gamma	Terminal methyl protons of alkyl sidechains three or more positions from an aromatic ring

* Data provided by CONSOL Inc.

1. $\frac{1}{2}$ 2. $\frac{1}{2}$ 3. $\frac{1}{2}$ 4. $\frac{1}{2}$ 5. $\frac{1}{2}$ 6. $\frac{1}{2}$ 7. $\frac{1}{2}$ 8. $\frac{1}{2}$ 9. $\frac{1}{2}$ 10. $\frac{1}{2}$

0667 129 444 72191 8 201-107-20 707249 00000 P=1.03

[illegible]

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* RUN # 195 OCT 1, 1981 16:08:08
START

STOP

RUN# 195 OCT 1, 1901 16:08:08

AREA%

RT	AREA	TYPE	WIDTH	AREA%
.808	20174928	PB	.034	73.21597
1.358	800	PB	.021	.00290
1.538	8447	PB	.016	.03065
1.777	5135	PB	.018	.01864
2.009	831	PB	.022	.00302
2.523	3532	PB	.027	.01282
15.499	22953	PV	.147	.08338
17.760	6697933	BV	.444	24.30718
17.866	30991	VB	.034	.11247
18.051	2031	PB	.056	.00737
19.083	6881	BV	.054	.02497
19.205	5473	VB	.072	.01986
19.753	4034	VB	.107	.01464
21.794	2397	BV	.058	.00870
22.764	135983	PB	.076	.49349
23.755	3905	PB	.051	.01417
26.635	3996	PP	.058	.01450
26.888	19144	PP	.086	.06947
27.211	261280	PB	.104	.94820
41.900	2373	BB	.069	.00861
42.446	2527	BB	.069	.00917
43.660	6933	PV	.119	.02516
44.700	115934	BV	.104	.42073
44.827	16188	VV	.061	.05875
45.089	5574	VB	.095	.02023
45.557	7315	VV	.127	.02655
46.058	7835	PB	.086	.02862

TOTAL AREA=2.7555E+07

MUL FACTOR=1.0000E+00

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DATE

FILMED

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END