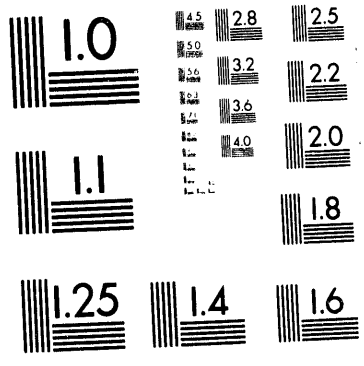
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1 of 1

DOE/PC/91055-T5

THE ROLE OF THE RESID SOLVENT IN COPROCESSING WITH FINELY DIVIDED CATALYSTS

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Introduction

The research performed this quarter involved evaluating the resid as the solvent in coprocessing. Since the objective of this research contract is to determine if the naphthenic portion of resids is able to transfer hydrogen to coal, the resid was fractionated in order to obtain different compositional fractions for liquefaction reactions. In order to evaluate different fractions of resids, the fractions must first be separated by liquid chromatography. The literature was surveyed as described below to determine the most feasible of effecting the separation. Methods used to analyze the fractions were also examined. On the basis of the information obtained, an experimental procedure was developed for separating the resid into fractions and then analyzing the fractions by Fourier transform infrared spectroscopy (FTIR) and by ^{13}C nuclear magnetic resonance.

Background

The objective of this literature review is to describe possible methods for separating resids into saturate and aromatic fractions and for obtaining detailed compositional information on the resids and their fractions. Some preparative chromatographic separation methods are also reviewed. The analyses of resid compositions by infrared spectroscopy (IR), mass spectrometry (MS), ^{1}H and ^{13}C nuclear magnetic resonance (NMR) are also included.

The increasing rate of energy consumption requires that coal and petroleum resids be further processed and converted into liquid fuels via feasible treatment processes. Compared with other fossil fuels, such as coal, petroleum resids are rich in hydrogen content and thus can

potentially donate hydrogen to coal when resid and coal are reacted together; this simultaneous reaction constitutes the basis of coal-resid coprocessing.

Many coprocessing studies have demonstrated that simultaneous upgrading of both resid and coal into liquid fuels is feasible.[1,2] For example, naphthenic model compounds, such as perhydropyrene, have been shown to be able to donate a small amount of hydrogen to coal in coprocessing.[3] This potential donation is encouraging since resids contain rich naphthenic components. Nevertheless, resids are more complicated mixtures of hydrocarbons and heteroatoms than the model compounds used to simulate them in studies, so that the role of resids and the mechanisms of hydrogen transfer in coprocessing must be determined. The difficulty partly arises from insufficient knowledge of resid compositions, e.g., the structures and the amount of naphthenes, hydroaromatic, aromatics, and heteroatoms in the resid. Although qualitative characterization of resids has been previously performed by IR,[7] quantitation of different types of hydrogen in the resid that can be transferred is still difficult.[13] With the advent of ^{1}H NMR and Fourier transform ^{13}C NMR, better methods for analyses of skeletal carbon-hydrogen groups have become available.

Before the resid is subjected to sophisticated structural analyses, the resid is usually separated into more specific fractions containing similar chemical structures. The subfractions are classified as saturates, hydroaromatics and aromatics. The separation is carried out by preparative liquid chromatography with silica gel as stationary phase. For the purpose of this survey of background information, an overview of preparative chromatography is described first, followed by an overview of the analyses of the subfractions of resids by IR, MS, ^{1}H NMR, and ^{13}C NMR.

Preparative Liquid Chromatography

Resids are high boiling point mixtures of naphthenes, hydroaromatics and aromatics. Resids also contain heteroatoms like O, S, and N that together amount to 6 wt% of the total resid. The contents of heteroatoms in resids vary with different types of resids. For example, oxygen contents vary from 0.3-4.9 wt%, sulfur contents vary from 0.3-10.3 wt% and nitrogen from 0.6-3.3 wt%.[18]

Resid is usually separated by preparative liquid chromatography before further analyses. All the preparative liquid chromatographic methods reviewed in this survey[4-8,10,11] are basically the same: resid is dissolved in nonpolar and polar solvents sequentially, eluted from a silica gel or alumina gel packed column, and collected as the said fractions. The commonly used packing substrates in the preparative chromatographic column is silica gel, although alumina gel is used occasionally. These substrates must be activated for at least 24 hr at elevated temperatures (>225 °C) before being used.

In all of the surveyed preparative liquid chromatographic methods,[7-9] the sample resids to be analyzed are first dissolved in a small amount (10-20 ml) of nonpolar solvent, e.g., pentane or cyclohexane. After the column is prewetted by the nonpolar solvent, the dissolved sample resid is added to the top of the column. Then fresh nonpolar solvent with a volume of 200 ml, which is contained in a reservoir mounted on the top of the column, is added onto the column successively. When resid molecules contact the porous silica gel particles, the polar aromatics are more likely to be adsorbed on the silica gel particles than the nonpolar saturates; therefore, the saturate compounds elute from the column first. After the nonpolar solvent in the reservoir has completely passed through the column, a polar solvent such as chloroform, benzene, ethyl ether,

or alcohol is added to the reservoir and elutes through the column. The eluates are collected as the aromatic fraction. If the cut point between the different fractions is well controlled, the resid can be separated into the desired fractions with little contamination from the other fraction.

Qian et al[4] examined structural parameters of some petroleum aromatic fractions by ^{1}H NMR/IR and ^{13}C plus ^{1}H NMR. In their study, the resid was treated by n-heptane at 45 °C, then the heptane solubles were subjected to a separation using a silica gel liquid chromatographic column at a solute/solvent weight ratio of 1:100. The saturate fraction was collected with heptane as eluent and the aromatic fraction was collected using benzene. The eluates were analyzed by NMR and IR. The analytical range was spread over 150 ppm with ^{13}C NMR and 4,000-600 cm^{-1} with IR. The results of NMR and IR showed that the separation was acceptable in that the saturates were separated from the aromatics. In their report, no operating parameters, such as column length, radius, and substrate packing weight, were reported.

Rahimi et al[5] studied the hydrogen donor ability of oils/bitumen and its effect on coal dissolution by using sulfur as a hydrogen acceptor and ^{13}C NMR as an analysis tool. In their study, the pentane soluble fractions of the resids were separated into saturates, aromatics and polars on a silica gel column. The saturates were defined as pentane eluate; the aromatics were defined as toluene eluate; and the polars were defined as methylene chloride eluate. The column was back flushed with methyl-tert-butyl ether in order to remove any residual materials from the column. The saturate fraction and the original samples (asphaltene free) were subsequently analyzed by ^{13}C NMR. The amount of transferable hydrogen was calculated from the integrated intensities in the 21-37 ppm range, the carbon contents of the original and the saturate fractions, and the weight percent of the saturate fractions. The fractions obtained were more detailed and

specific than those obtained by Qian.[4] The authors also used elemental sulfur as a hydrogen acceptor and measured the amount of hydrogen transferred from resid to sulfur. The intention was to compare the amount of transferred hydrogen obtained using the sulfur method and using the ^{13}C NMR method.

In preparative chromatography, carefully selected model compounds are required to verify that the separation is successful and applicable to the more complicated resids. This process was well illustrated by Aiura et al.[6] In their study, two mixtures that were composed of model compounds chosen from naphthenes to aromatics in a wide polyaromatic ring range were used. Then the theoretical transferable hydrogen of the mixtures was calculated as a reference to examine the accuracy of the results obtained by ^{13}C NMR. When the mixtures were analyzed by ^{13}C NMR, an acceptable agreement between the theoretical amount and the analyzed result of transferable hydrogen was observed. Then a 1.5 g resid sample was charged on a preparative chromatographic column packed with 70 g of silica gel using equivalent conditions as the model separation. After eluting the resid sample with 200 ml of cyclohexane, the eluates were concentrated below 50 °C in vacuo for weighing.

Some researchers[7-8] were not satisfied with the simple preparative chromatography in which eluates were classified only as saturates and aromatics. They performed more thorough and specific separation by sequential ion-exchange, coordination, and adsorptive chromatography. The advantage of these methods was that the nature of resids were more likely to be elucidated without interference of other fractions. These sequences removed nonhydrocarbons such as acids, bases and neutral-nitrogen fractions before the resids were further separated by preparative chromatography and enabled further analysis of the resulting fractions.

Jewel and coworkers[4] developed a separation scheme to characterize[4] heavy end petroleum distillates with ion-exchange, coordination and adsorptive chromatography. In their study, the anions were first removed from the resid with anion-exchange resin (Amberlyst-29 resid), then the cations were removed with cation-exchange resin (Amberlyst 15). The anion and cation-free sample was then contacted with ferric chloride supported on Attapulgus clay to remove the neutral nitrogen fraction. Ion-exchange procedures were performed in a column that was 1.4-1.75 cm in diameter and 116 cm in length. With the same size column, the sample that was free of anions, cations and neutral nitrogen fraction was separated by a silica gel packed column with pentane and methanol as eluents, into saturates and aromatics, respectively. The components separated by preparative chromatography were monitored with a UV detector at 270 nm. The authors claimed that the advantage of the separation scheme was its reproducibility (±4%) and recovery (96% and higher).

Hirsch et al.[8] examined the process of separating petroleum distillates (b.p. 330-540 °C) into saturates, monoaromatics, diaromatics, and polyaromatics. In their study a dual packed column (1 in. by 8 ft.) was used for this purpose; the top half of the column was packed with silica gel and bottom half with alumina gel, which were activated at elevated temperatures of 400 °C and 265 °C, respectively, for 16 hr. The authors explained that if the partially deactivated silica gel was used as proposed by Snyder[14] to achieve some degree of adsorption isotherm linearity, the sample adsorptive capacity of the gel would be reduced by 10 to 100 times, and the retention volumes would be too close to control the cut points. In their experiment, the cut points of the desired fractions were monitored by radioactive tracer techniques. The report claimed that there were advantages of subdividing the aromatics and polar compounds: The three individual

aromatic fractions were easier to analyze by low resolution mass spectrometry; and further separation by gel permeation chromatography (GPC) and other techniques was much less complicated. However, this separation method was tedious and time consuming because the total solvent volume, up to 10 L, was required at 200 ml/hr in the large column (1 in. in diameter and 8 ft. in length), although the processing capacity was high (25-50 g).

Preparative chromatography can be readily performed by ASTM standard test method D2549.[9] The summary of this method is (1) A weighed amount of sample is charged to the top of a glass chromatographic column packed with activated bauxite and silica gel. n-Pentane is added to the column to elute the nonaromatics. When all of the nonaromatics are eluted, the aromatic fraction is eluted by additions of diethyl ether, chloroform, and ethyl alcohol. (2) The solvents are completely removed by evaporation, and the residues are weighed and calculated as the aromatic and nonaromatic fractions of the sample.

Analysis of Resid Fractions

Structural information of resid can be obtained when the subfractions arising from preparative chromatography are analyzed further by advanced methods. These analysis methods are IR, MS, and ^{1}H and ^{13}C NMR.

1. **Infrared Spectroscopy (IR)**

Of all the current instrumental analytical methods capable of precise molecular structural analysis, ^{1}H and ^{13}C NMR are the most powerful. However, in comparison with NMR, IR is easier and quicker to operate.

Since different C-H bond vibrational and rotational movements can be detected by IR, the relative amount of methyl, methylene, and methine groups present in a sample is obtainable by IR. Qian[4] used IR as an analytical method and resolved the combined equations proposed by Yen et al.[15] and Haley[16] separately so as to obtain the molecular average parameters of resid. The parameters included total carbon atoms per average molecule, H/C atomic ratio of alkyl substituents, aromaticity index, and aromatic rings per average molecule, etc. The combined equation correlated the absorbencies of two peaks that appeared at 2920 cm^{-1} and 1380 cm^{-1}. The peak at 2920 cm^{-1} was assigned to C-H stretching of the methylene group and the peak at 1380 cm^{-1} was assigned to C-H symmetrical bending vibration of the methyl group. The authors compared the results obtained from ^{1}H NMR/IR, ^{13}C coupled ^{1}H NMR and that from Brown-Ladner methods. It was concluded that ^{1}H NMR/IR was the most precise method for obtaining average molecular parameters. But for thorough characterization of resid, ^{13}C coupled ^{1}H NMR was the best to date.

The IR spectra of saturates differ from those obtained from aromatic fractions. For aromatics, absorbencies will occur at 3030 cm^{-1} for =C-H stretching vibrations and at 1650-1450 cm^{-1} for the ring C=C vibrations. Absorbencies for saturates and naphthenics occur in the range of 1460-1467 cm^{-1} for methylene scissoring vibrations, but seldom is visible below 900 cm^{-1} for C-H out-of-plane bending.[17] To determine if the separation of resids by preparative chromatography is acceptable, the IR aborbances of the spectra from the different fractions are determined and compared. The spectrum from the saturate fraction should not contain any absorbencies from aromatic compounds.

2. Mass Spectrometry

Mass spectrometry coupled with gas chromatography is seldom used in the characterization of resids, although other methods such field ionization mass spectrometry can be used. As stated by Clark[10] "NMR is a convenient method of measuring the changes in solvent composition that result from hydrogen donation to coal during extraction. The use of gas-liquid chromatography and mass spectrometry for this purpose is difficult as these techniques measure individual constituents rather than average properties." However, if the appropriate method and relationship are utilized, MS is able to identify molecules, as demonstrated by Jewel[7] as follows.

In the study of Jewel and coworkers,[7] MS were employed to characterize the saturate and the aromatic fractions of four heavy-end petroleum distillates. The characteristics of the distillates measured by MS were the numbers of rings present in the saturate and the aromatic fractions, the weight distributions of each composites containing the same ring numbers, and the amount of sulfur present in the distillates.

The authors used different methods to characterize the saturate and the aromatic fractions with MS. For the saturate fraction, the method developed by Hood and O'Neal was used. This method was a high-ionizing voltage, low-resolution method and allowed the determination of zero to six condensed-ring saturates. For the aromatic fraction, one low-voltage and two high-voltage methods were used. The two high-voltage methods were developed by Hastings and Robinson and Cook, and allowed the determination of 12 aromatic compound types, three sulfur aromatic compound types and six unidentified types.

On the basis of the results of the saturate fraction, the authors claimed that the application of Hood and O'Neal's method to Wilmington heavy-end distillate was in agreement with the results obtained by other workers[9] and by using extensive NMR in the author's lab. For the aromatic fraction, the results were given in the average derived from the three methods: (1) Hasting's, (2) Robinson and Cook's, and (3) low-voltage method, because none of the three was reliably accurate. The deviation of the analyzed parameters, i.e., number of rings in the saturate and the aromatic fractions and the weight percent of the composites containing the same rings numbers, were within 20% for most of the hydrocarbon components present.

3. **^{1}H NMR and ^{13}C NMR**

Of all the instrumental analytical methods capable of precise molecular structural analysis, ^{1}H NMR and ^{13}C NMR are the most powerful. Between ^{1}H NMR and ^{13}C NMR, ^{1}H NMR is more convenient for characterizing aromatic heavy fractions of resids if the proper correlation between hydrogen and skeletal carbons are known.[4] But the information of skeletal carbon atoms, especially those not containing hydrogen atoms, such as bridgehead aromatic carbon, carbonyl and aromatic ether, cannot be readily obtained from ^{1}H NMR. This problem was solved by the development of ^{13}C NMR.

Not long after ^{13}C NMR was recognized as a tool for characterizing the carbon skeleton in organic compounds, the coupling of protons, as well as the nuclear Overhauser enhancement effect and long thermal relaxation times, was seen as obstacles to its application. Fortunately, with the advent of Fourier transform NMR and proton decoupling, it was possible to obtain the desired structural information with ^{13}C NMR.

The use of a relaxation reagent and the gated decoupling technique greatly shortened the thermal relaxation time from 1 min to 0.1 sec and suppressed the Overhauser enhancement effect.[11]

In 1979 Snape and Ladner[12] proposed a plan to assign ^{13}C NMR chemical shifts based on the published data to date and solved the problems of insufficient data that had hampered the application of ^{13}C NMR to coal-derived materials. The authors claimed that the plan was also applicable to a majority of coal-derived materials and resids. This publication was the underpinning of later ^{13}C NMR analysis work.

Qian[4] performed ^{1}H NMR on petroleum aromatic fractions. Different proton types were defined by the following chemical shift ranges (relative to TMS): aromatic protons, 6.35-9.0 ppm; α-protons on alkyl side chains, 2.0-4.0 ppm; β-protons on alkyl side chains, 1.05-2.0 ppm; γ-protons on the terminal CH_3 groups, 0.5-1.05 ppm; and olefinic protons, 4.0-6.0 ppm. The authors also performed ^{13}C NMR with $CDCl_3$ as a solvent and $Cr(AcAc)_3$ as the relaxation reagent and obtained the spectra in which the aliphatic carbon absorption ranged from 10 to 70 ppm and aromatic carbon absorption ranged from 110 to 160 ppm.

To obtain the transferable hydrogen in hydroaromatics by ^{13}C NMR, the intensities in 21-37 ppm were integrated and then calculated with the carbon contents in the original and saturate fractions and the weight percent of saturate fraction.[5,6,10] The equation of transferable hydrogen content (TH) was given as following:

$$TH(wt\%)=[(CxCha-SaxCsxScx10^{-2})/12]x10^{-2}$$

where: C and Sc = carbon content (wt%) in the original solvents and in the fractionated saturates, respectively; Cha and Cs = the integrated intensities (%) in 21-37 ppm range in the spectra of the original solvents and fractionated saturates, respectively; and Sa = the wt% of the saturate fraction.

In order to obtain a rapid and automatic analysis method using ^{13}C NMR for resids, Bouquet and Bailleul[13] proposed a routine method in which no assumptions on chemical shifts were needed. They employed two well established pulsed techniques, i.e., inverse gated decoupling with a relaxation reagent and spin echo experiments with a relaxation reagent. This method applied to four resid samples and was verified by ^{1}H NMR, with standards, demonstrating that the method is able to determine the hydrocarbon unit (CH_n groups, n=0-3). Still, a long time was needed to conduct the analysis; vacuum resid required 2 hr and asphaltenes 10 hr. This method also required a slow spectra editing process that was less than 6 hr for vacuum distillates and more for resids.

Summary. Thorough and detailed characterization of the structural groups in resid is important for the understanding of coal-resid coprocessing. A prerequisite to characterizing resid is to separate resids into fractions from saturates to aromatics. From the literature surveyed, it is concluded that the separation can be carried out by preparative chromatography as described in ASTM D 2549. Some simplification and alteration are applicable, such as changing the column length and substrate weight. The quality of the separation can be achieved by controlling the cut points between different fractions using IR as monitor.

The structural information of resids, e.g., aromacity and CH_n (n=0-3) content, can be carried out by ^{1}H NMR and ^{13}C NMR alone, or with the help of IR. Since ^{13}C NMR can directly

analyze the structures of skeletal carbons, it is theoretically feasible but time consuming. ^{1}H NMR is a simpler and easier method if the relation between hydrogen and carbon atoms is known, especially when combined with IR.

EXPERIMENTAL

Materials. Maya resid was obtained from Amoco and was used as the test resid in this study. The eluting solvents used in the liquid chromatographic separation were HPLC grade cyclohexane, chloroform, and THF obtained from Fisher Scientific. The solid packing, silica gel, had a mesh size of 100 to 200 and was obtained from Aldrich Chemical Company. The model compounds, anthracene (99.9% purity), dihydroanthracene (97% purity), hexahydroanthracene (99+% purity), and pyrene (99+% purity), were used as received for a test liquid chromatographic mixture. All model compounds were obtained from Aldrich Chemical Company.

Chromatographic Separation. Maya resid was fractionated initially into hexane and toluene soluble materials. To effect the separation, 150 ml of hexane were added to 2.0 g Maya resid and the mixture of hexane plus resid was sonicated. The hexane and resid were then centrifuged at 4,000 rpm for 10 min. After centrifugation, the liquid layer at the top of the bottle consisting of hexane and hexane soluble resid was removed. At this point another 150 ml of hexane was added to the resid and the process was repeated twice until a total of 450 ml of hexane had been used. The hexane was removed by using a rotary evaporator. The hexane solubles were dried in a vacuum oven at 60 °C for 12 hr. The material remaining was defined as hexane solubles. The hexane soluble fraction was then separated further by preparative liquid chromatography into solubility fraction as described later in the experimental section.

For the liquid chromatographic separation, silica gel was activated in a drying oven at 240 °C for at least 24 hr before use. The pyrex chromatography column was washed with detergent and water and was thoroughly rinsed with distilled water prior to use. The silica gel was poured into a pyrex column with an Al-Mg filter at the bottom of the column to retain the silica gel and was packed by tapping the column gently. Two different sized chromatography columns were used during this quarter, one column was 76.2 cm long and 9.5 mm ID, while the other column was 30 cm long and 9.5 mm ID. The silica gel column was wetted with cyclohexane prior to introduction of the model test mixture.

The first experiment performed involved evaluating two model test mixtures which were composed of naphthenic, hydroaromatic and aromatic species. Each test mixture contained different amounts of each species. The species contained in the test mixtures were decalin, anthracene, dihydroanthracene, octahydroanthracene and pyrene. The procedure used for the separation was to dissolve 2.0 g of model mixture in 5.0 ml of cyclohexane. The model test mixture was placed on the top of the prewetted silica gel column. Two hundred ml of cyclohexane are then eluted through the column and the eluate was collected as saturates. When the cyclohexane had passed through the column, 200 ml of chloroform were added to the column and the eluate collected was labeled aromatics. The eluate collected immediately after the chloroform was added was defined as intermediates. The recoveries from model mixture No. 1 and No. 2 were 100 and 99.5%, respectively.

The elements obtained from the chromatography column was analyzed by gas chromatography using a Model 3300 Varian GC equipped with an Al-clad HT-5 fused silica column from SGE and FID detection. The temperature program employed in the analysis was a

column initial temperature of 60 °C, an initial hold time of 5 min, a final program temperature of 190 °C and a temperature program rate of 2.5 °C/min. A second program increase of 15 °C/min was then instituted ending at a final temperature of 320 °C. The species in the model mixture were quantitatively analyzed by using the internal standard technique with biphenyl as the internal standard. The recoveries and separations of the components agreed better with the theoretical calculations where the longer column was used.

The hexane soluble fraction of the resid was then separated using silica gel as the column support material and three different solvents, cyclohexane, toluene, and THF as the eluting solvents. One separation was performed with the 30 cm column and four separations were performed with the 76 cm column. Two grams of the hexane soluble fraction from Maya resid was dissolved in 10 ml of cyclohexane and was placed on top the silica gel column prewetted by cyclohexane. Two hundred ml of cyclohexane was then eluted through the column. The eluate was collected and labeled as saturates. After cyclohexane had passed through the column, 200 ml of chloroform was added and the eluate was collected and defined as aromatics. The eluate that eluted immediately after the solvent was switched from cyclohexane to chloroform was collected separately and was defined as intermediates which, in fact, contained aromatics. Any of the hexane soluble material that remained adsorbed on the silica gel surface after chloroform was eluted was removed from the column by eluting THF. The eluate fractions underwent rotary evaporation and were then dried in a vacuum oven at 60 °C for 24 hr. The dried fractions were then weighed and recoveries calculated.

Analysis of Resid Samples by FTIR. Four different resid samples were analyzed by FTIR: whole resid, saturate fraction, aromatic fraction and the intermediate fraction. The

were kept in 20 ml sample vials and dried in a vacuum oven at 60 °C until a constant weight was obtained. The samples were diluted to a concentration of 0.025 g/ml by adding the necessary amount of THF to achieve that dilution. The samples of resid fractions were prepared as a thin film on a NaCl salt plate. To prepare the NaCl salt plate for infrared analysis, the NaCl salt plate was washed with THF and dried in an oven at 60 °C for 15 min. The salt plate was then removed from the oven and placed in a desiccator where the salt plate was allowed to cool for 5 min. The NaCl salt plate was then placed in the FTIR and a background spectrum was scanned. The thin film was prepared by placing 12 drops of sample, diluted in THF onto the salt plate. The introduction of the sample was done methodically to insure that an even film was produced. The thin film was prepared on the salt plate in the fume hood so that a substantial amount of the THF evaporated as the THF and resid solution was placed on the plate. The wet sample on the salt plate was dried in an oven at 60 °C for 15 min; the salt plate was then removed and allowed to cool in a desiccator for 5 min. The thin film was then analyzed by FTIR by placing the salt plate in the cell holder of the instrument. The sample was scanned 12 times and the spectrum was obtained and recorded. Each fraction was duplicated and each thin film was analyzed twice. Subsequent samples were prepared after washing the NaCl salt plate with THF.

Analysis of Resid Samples by ^{1}H and ^{13}C NMR. The whole resid and resid fractions were analyzed by ^{1}H and ^{13}C NMR. ^{1}H NMR and ^{13}C NMR samples were prepared by dissolving 0.4 g of resid or resid fraction in 3 g of $CDCl_3$ (99.5% from Aldrich). TMS was used as an internal reference. The resid sample was 10 to 15 wt% while the TMS concentration was 2 wt%. For the analysis 0.5 ml of sample was placed in a 5 mm I.D. NMR tube for analysis. A Bruker

AC250 FT NMR spectrometer was used for the ^{13}C NMR analysis. The parameters set for the analysis are given below:

Frequency:	62.9 MHZ
Pulse Width:	2.3 μs
Data Points:	32,000
Spectrum Width:	300 ppm
Filter Band Width:	25,000
Pulse repetition:	1.8 sec.

RESULTS AND DISCUSSIONS

The purpose of the research performed this quarter was to develop methods of separating resids in order to obtain samples in which the naphthenes were concentrated so that liquefaction reactions could be performed. This quarter's work consisted largely of developing a means of separating the resid into fractions and, subsequently, analyzing those fractions as well as developing an experimental matrix by which to determine the effect of different resid fractions on the conversion of Illinois No. 6 coal. The literature was surveyed to determine the most expeditious procedure to effect the separation. The first set of experiments that was performed involved model mixtures which tested the efficacy of the separation method. The second set of experiments involved performing the separation of resid.

Separation of Model Mixtures. Two model mixtures were prepared which contained a naphthene, decalin; hydroaromatics, 9,10-dihydroanthracene and hexahydroanthracene; and aromatics, anthracene and pyrene. These model mixtures were separated on a 30 cm and a 76 cm

silica gel liquid chromatography column. Model mixture No. 1 contained 70.3% naphthene and was separated on the shorter column while model mixture No. 2 contained 40.4% naphthenes and was separated on the longer column. The separation was effected by first eluting with cyclohexane and then with chloroform. The amount of each model compound obtained in each fraction was determined by gas chromatography. The recoveries of the different model compounds were nearly 100%. The deviations of these recoveries from 100% resulted in error in recovery of the material as well as from inaccuracies in the gas chromatographic response factors.

The results obtained from the liquid chromatographic separation of two model mixtures are given in Tables 1 and 2. The cyclohexane eluted over the silica gel was very effective in separating the decalin from the hydroaromatic and aromatic species. This separation was effective in both the shorter and longer columns. The longer column, however, appeared to separate more effectively the aromatics.

The theoretical weight percent of saturates in model mixture No.1 was 70.3%; the weight percent of saturates obtained from the separation was 67.1%, which resulted in 95.5% of the decalin being recovered in saturate fraction. The theoretical weight percent of saturates in model mixture No. 2 was 40.4%; the weight percent of saturates obtained from the separation was 32.4% which resulted in 80.1% of the decalin being recovered in the saturate fraction. After these analyses the hexane soluble fraction of the resid was separated on both the 30 and 76 cm chromatographic silica gel column.

Separation of the Hexane Soluble Fraction of Maya Resid. The hexane soluble fraction of Maya resid was separated using a 30 cm silica gel chromatography column. The separation

achieved is presented on Table 3. The appearance of the different bands eluting down the column indicated that incomplete separation of the saturates and aromatics had occurred. Therefore, separation on the 70 cm column was begun.

The separations of hexane soluble Maya resid using the 70 cm column are presented in Table 4. The separations are numbered in sequential order. Separations 2, 3, and 4 gave fairly high recoveries, 94 to 97%, and the results were fairly consistent, though more consistency in the separation is being sought in the separations performed in the upcoming quarter.

Analysis of the Resid Fractions. The resid fractions were analyzed by FTIR analysis and by ^{1}H and ^{13}C NMR. The eluate fractions obtained by liquid chromatography were cast into a thin film and analyzed by FTIR. Representative spectra obtained for the different fractions are presented in Figures 1-4. The primary peaks obtained in the spectra are presented in Table 5. The wavenumbers and intensity for each peak of each fraction are given; however, the intensity values should only be compared within a given fraction. The peaks obtained in every fraction were nearly identical and all result from C-H absorbances. A summary of characteristic infrared absorptions of methyl, methylene, and aromatic absorbances are given in Table 6. The peak at 2922, 2852 and 1456 cm^{-1} are all representative of $-CH_2$ vibrations while those at 2949-2951, 1375, and 1456 cm^{-1} are representative of $-CH_3$ vibrations.[17]

Since the direct measurement of the intensity of infrared bonds could not be compared from fraction to fraction because of differences in the thickness of the thin films of each fraction, two different methods for the comparison of the intensities of the IR absorbance bands have been developed. At this time, both methods will be included, but as more separations are achieved and analyzed next quarter, one method of comparison will be chosen. In Table 7a, the absorbance of

each particular bond is divided by the sum of the absorbances of all of the bands. In Table 7b, the absorbance at ~2950 cm^{-1} was taken as 1.00 and the relative ratios of the absorbances at the other wavenumbers were calculated. The differences among the peak intensities in the different fractions are most easily observed in Table 7b. The 2922 cm^{-1} band which represents symmetric vibration of H in $-CH_2$ was stronger in the saturates fraction than in either the aromatic or intermediate fractions.

In the IR spectra of all the fractions, the peak at 2920 cm^{-1} was more intense than any of the other peaks. The second strongest peak was 2852 cm^{-1} which is the symmetric vibration of H in $-CH_2$. The methyl peak at 2950 cm^{-1} was less intense than the methylene peak at 2922 cm^{-1}. The spectra indicated that Maya contained appreciable amounts of methylene groups present either as straight chain alkanes or naphthenic hydrocarbons.

^{13}C NMR of Chromatographic Fractions. Although no appreciable differences were observed among the FTIR spectra of the saturate and aromatic fractions, the chemical shifts observed in the ^{13}C NMR spectra for the two fractions were quite different as shown in Table 8. Maya resid was obviously separated into two distinct fractions as can be observed by comparing the quantity of peaks between 14 and 37 ppm. The saturate fraction had 12 peaks while the aromatic fraction had four peaks. The relative intensity of the peaks along with an assignment is given in Table 9. Using the 14.1 ppm peak as the reference shows that parent resid usually had the most intense peaks although the intensity of the saturate peaks was very similar. The intensity of the peaks in the aromatic was less. Further experimentation is underway using ^{13}C NMR as an analysis tool for the fractionated resid.

SUMMARY AND FUTURE WORK

The research this quarter resulted in the development of a chromatographic separation and an analysis scheme which enables preparation of samples for coal liquefaction experiments. An experimental matrix (Table 10) has been developed to study the role of resids in coprocessing.

The first set of experiments will be performed by reacting resids with hydrogen acceptors. Anthracene will be used as a hydrogen acceptor and will be reacted with resid fractions that include hexane soluble oils and hexane insoluble asphaltenes as well as their combinations. Since naphthenic compounds are present in the oil fraction, the saturate fraction of the oil obtained by preparative liquid chromatography will be also employed to evaluate its effect on coprocessing. The aromatic fraction as well as combinations of the saturate and aromatic fractions will also be used. After the anthracene experiments are completed, coal will be introduced into the system as a hydrogen acceptor in order to evaluate the effect of the different resid fractions on coal.

The reactions will be conducted in stainless steel tubular microreactors. The products will be analyzed by several methods including (1) determining the amount of hydrogen transferred from the various resid fractions to anthracene and (2) determining the conversion of coal and the products produced from the coal.

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Figure 1. Saturate Fraction of Maya Resid.

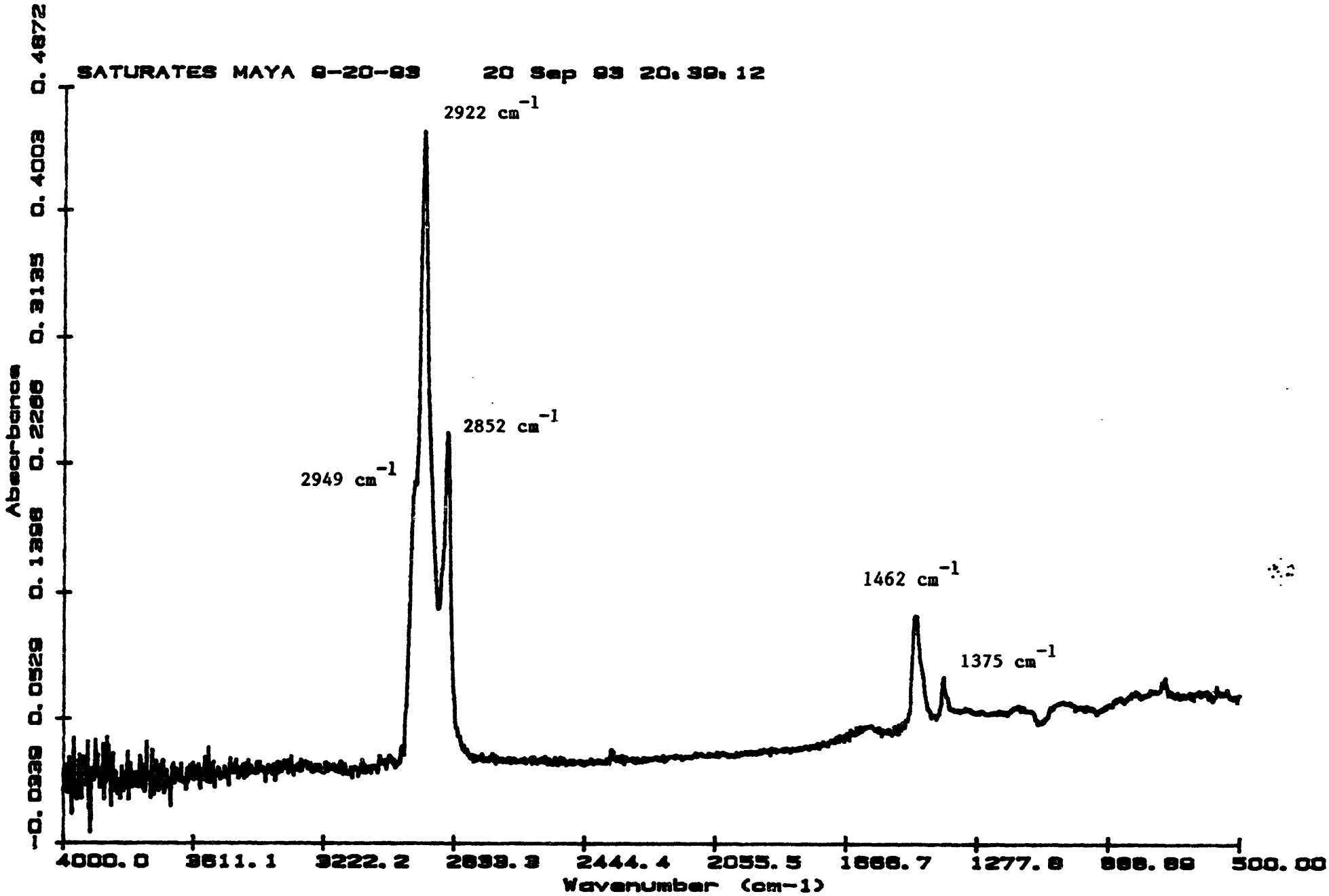

Figure 2. Aromatic Fraction of Maya Resid.

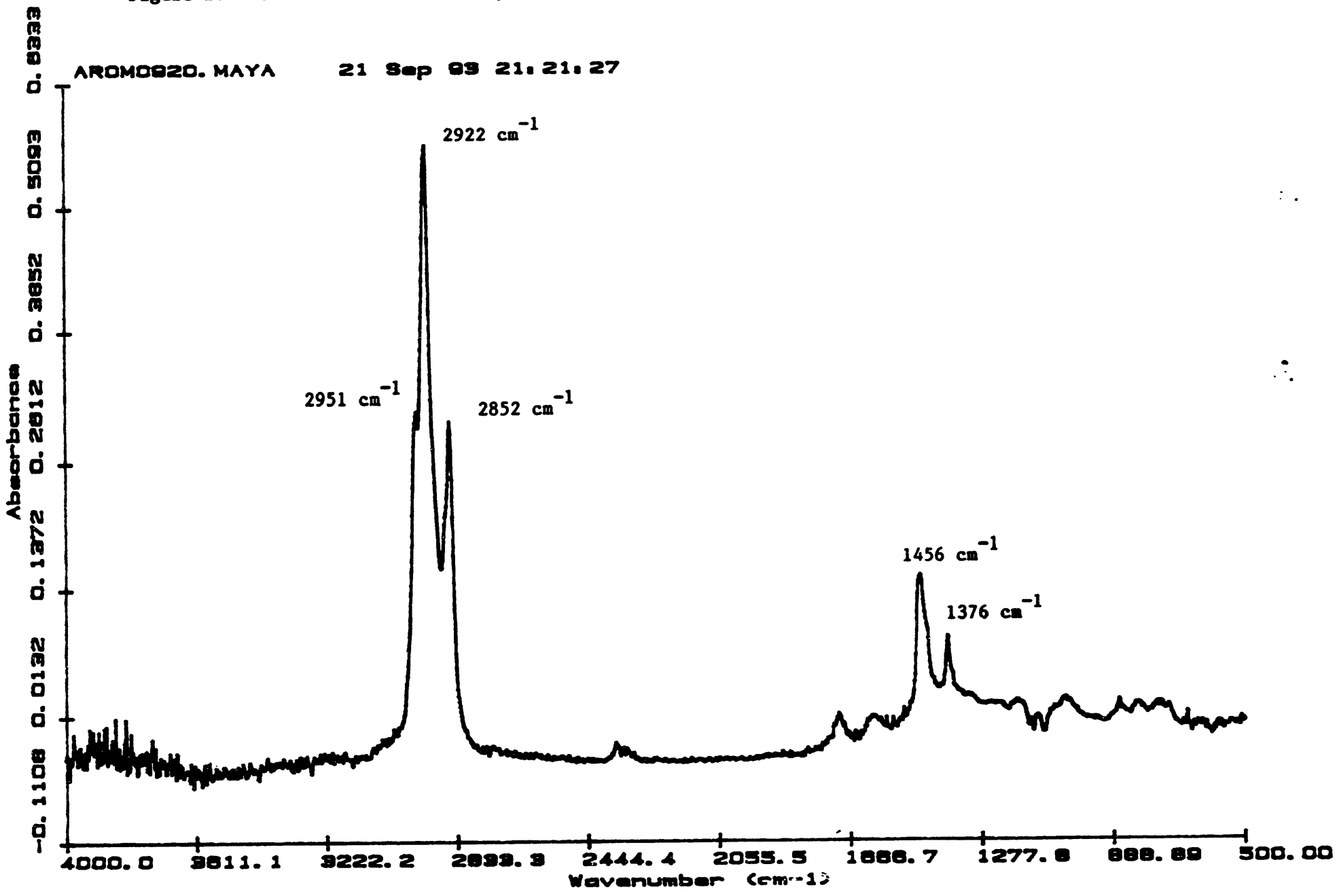

Figure 3. THF Eluate Fraction of Maya Resid.

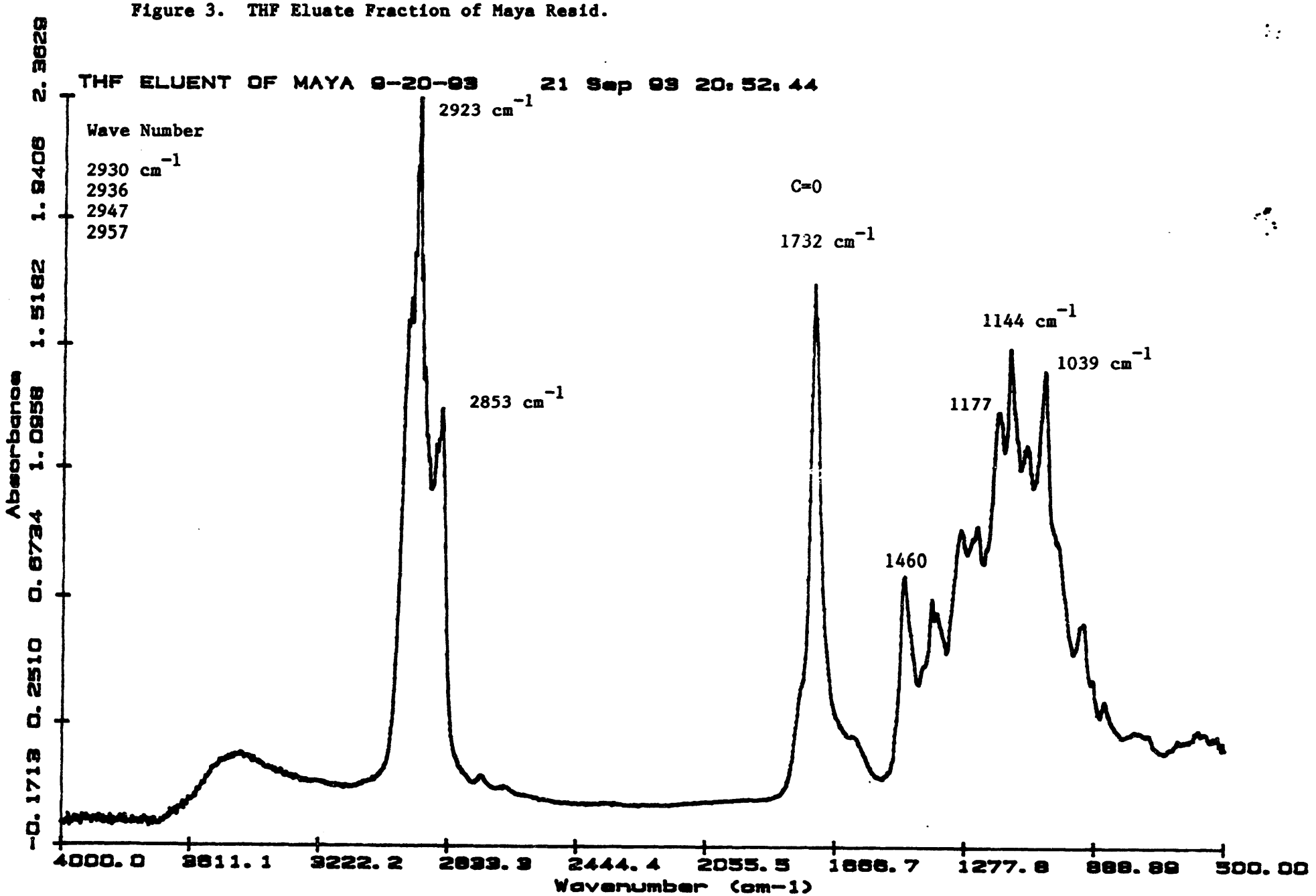

Figure 4. Intermediate Fraction of Maya Resid.

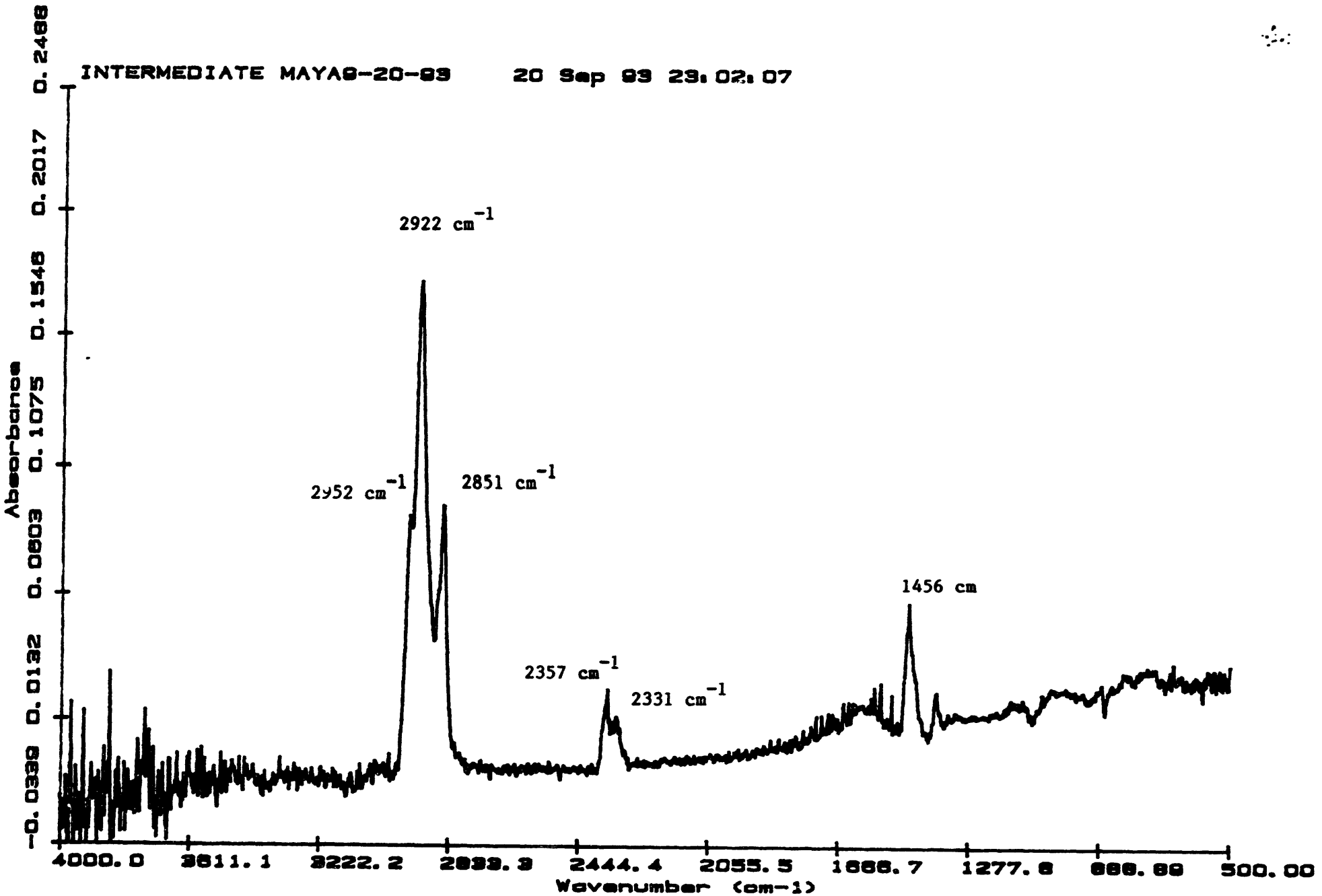

Table 1. Liquid Chromatography of Model Mixture No. 1.

Table 1a. Composition of Model Mixture No. 1

Model Compound[a,b]	DEC	DHA	HHA	ANT	PYR
wt%	70.3	5.5	4.6	9.8	9.7

[a]ANT=anthracene; DEC=decalin; DHA=dihydroanthracene; HHA=hexahydroanthracene; PYR=pyrene
[b]Total mixture weight=2.0041 g

Table 1b. Distribution of Model Mixture No. 1 Components after Chromatographic Separation[a]

Fraction	DEC	DHA	HHA	ANT	PYR
Saturates[b]	99.8	0.0	0.0	0.0	0.2
Intermediates[c]	12.3	18.0	13.9	26.8	28.9
Aromatics[d]	8.1	18.2	9.9	29.5	31.0
Component Recovery %	101.9	106.4	96.8	87.4	98.3

[a]Column length = 30 cm; silica gel loading = 12.6 g.
[b]Saturates are compounds eluted with cyclohexane.
[c]Intermediates are compounds eluted when chloroform begins eluting.
[d]Aromatics are compounds eluted with chloroform only; all cyclohexane has been removed from the column.

Table 1c. Fractional Distribution of Model Mixture No. 1

	Saturates	Intermediates	Aromatics
Theoretical wt% of Fractions	70.3		29.7
Recovered wt% of Fractions	67.1	31.2	1.7

Table 1d. Weight Percent of Each Compound Type Recovered

	Saturates	Intermediates	Aromatics
Wt% of Saturated Components Recovered in Each Fraction	95.4	31.2	1.7
Wt% of Aromatic Compound Recovered in Each Fraction	0.7	89.1	5.3

Table 2. Liquid Chromatography of Model Mixture No. 2

Table 2a. Composition of Model Mixture No. 2

Model Compound[a,b]	DEC	DHA	HHA	ANT	PYR
wt%	40.4	15.1	15.0	14.4	15.1

[a]ANT=anthracene; DEC=decalin; DHA=dihydroanthracene; HHA=hexahydroanthracene; PYR=pyrene
[b]Total mixture amount = 2.0012 g.

Table 2b. Distribution of Model Mixture No. 2 Components after Chromatographic Separation[a]

Fractions	DEC	DHA	HHA	ANT	PYR
Saturates[b]	99.0	-	-	-	1.0
Intermediates[c]	54.5	7.9	15.2	7.4	14.9
Aromatics[d]	1.3	26.0	23.8	24.9	23.9
Component Recovery %	100	98.4	98.2	98.6	100

[a]Column length = 76 cm; silica gel loading = 36 g.
[b]Saturates are compounds eluted with cyclohexane.
[c]Intermediates are compounds eluted when chloroform begins eluting.
[d]Aromatics are compounds eluted with chloroform only; all cyclohexane has been removed from the column.

Table 2c. Fractional Distribution of Model Mixture 2

	Saturates	Intermediates	Aromatics
Theoretical wt% of Fractions	40.4		59.6
Recovered wt% of Fractions	32.4	14.4	53.1

Table 2d. Weight Percent of Each Compound Type Recovered

	Saturates	Intermediates	Aromatics
Wt% of Saturated Components Recovered in Each Fraction	80.0	19.2	10.9
Wt% of Aromatic Compound Recovered in Each Fraction	1.1	10.9	87.8

Table 3. Preparative Chromatography for Maya Hexane Solubles Using a 30 cm Liquid Chromatography Column[a]

Fraction	Saturates[b]	Intermediates[c]	Aromatics[c]	Recovery
wt%	72.9	4.8	22.4	89.0

[a]Column length = 30 cm; silica gel loading = 12.6 g
[b]Saturates are compounds eluted with cyclohexane.
[c]Intermediates are compounds eluted when chloroform begins eluting.
[d]Aromatics are compounds eluted with chloroform only; all cyclohexane has been removed from the column.

Table 4. Preparative Chromatography for Maya Hexane Solubles Using a 76 cm Liquid Chromatography Column[a]

No.	Saturates[b] (wt%)	Intermediates[c] (wt%)	Aromatics[d] (wt%)	THF[e] (wt%)	Recovery (wt%)
1	45.4	40.7	13.8	ND[f]	79.1
2	59.4	23.3	19.5	ND	97.4
3	57.2	27.8	7.0	7.9	94.3
4	67.3	20.9	2.2	9.6	95.6

[a]Column length = 76 cm; silica gel loading = 36 g; ND = not determined
[b]Saturates are compounds eluted with cyclohexane.
[c]Intermediates are compounds eluted when chloroform begins eluting.
[d]Aromatics are compounds eluted with chloroform only; all cyclohexane has been removed from the column.
[e]THF eluent
[f]ND = not determined.

Table 5. Summary of Characteristic Infrared Absorptions

Functional Group	Frequency (cm-1)	Remarks
$-CH_3$ in alkane	1380-1370 (s)	symmetric C-H deformation
	2962±10 (s)	C-H stretching doublet
	1450±20 (m)	asymmetric C-H deformation
$-CH_2$ in alkane	2853±5 (s)	symmetric vibration of H atom
	2926±5 (s)	asymmetric vibration of H atom
	1465±15 (m)	C-H bending; sharp
-CH in alkane	2890±10 (w)	C-H stretching
C=C (nonconj.) in alkene	1670-1615	C=C stretching, intensity quite variable
C=C (conj.) in alkene	1600-1590	C=C stretching, intensity enhanced
aromatic ring vibrations C=C	1600, 1500 (s)	ring vibration due to the conjugated C=C bond

Note: * (s) = strong intensity; (m) = medium intensity

Table 6. IR Spectra of Different Fractions of Maya Resid

Fractions	Wave Number (cm^{-1})	Absorbance
Saturates	1375	0.084
	1462	0.125
	2852	0.247
	2922	0.456
	2949	0.214
Aromatics	1376	0.313
	1456	0.400
	2852	0.564
	2922	0.861
	2951	0.586
Intermediates	1456	0.058
	2851	0.095
	2922	0.175
	2952	0.090

Table 7a. Comparison of Infrared Absorbance Distributions of Maya Resid Fractions

Group	cm^{-1}	Saturates (%)	Aromatics (%)	Intermediates (%)
$-CH_3$	1376	7.5[a]	11.5	0
	1456	11.1	14.7	13.8
	2950	19.0	21.5	21.5
$-CH_2$	2853	21.9	20.7	22.8
	2922	40.5	31.6	41.9

[a] The number is the absorbance at 1376 cm^{-1} divided by the sum of absorbances at all wavenumbers of the specific fraction and multiplied by 100%. The absorbances are listed in Table 6.

Table 7b. Comparison of Absorbance Ratios of Maya Resid Fraction[a]

Group	cm^{-1}	Saturates	Aromatics	Intermediates
$-CH_3$	1376	0.39	0.53	0.00
	1456	0.58	0.68	0.64
	2950	1.00	1.00	1.00
$-CH_2$	2853	1.15	0.96	1.06
	2922	2.13	1.47	1.49

[a]The values were obtained by taking the absorbance at 2950 cm^{-1} as 1.00, and calculating the relative ratios of absorbances at other wavenumbers with respect to 2950 cm^{-1} in Table 6.

Table 8. ^{13}C NMR Chemical Shifts of Maya Resid and Saturate and Aromatic Fractions of Maya Resid

Fraction	Chemical Shifts (TMS=0)
Maya resid	14.1, 19.7, 22.7, 27.1, 29.4, 29.7, 30.1, 32.0, 34.3, 37.5, 158.9
Saturates	14.1, 19.8, 22.7, 24.5, 26.7, 27.1, 29.4, 29.7, 30.1, 32.0, 32.8, 37.1
Aromatics	14.1, 22.7, 29.7, 31.9

Table 9. Relative Intensity Ratios of ^{13}C NMR of Maya

Assignment[b]	Shift (ppm)	Maya	Saturates	Aromatics
end $-\underline{C}H_3$	14.1	1.00[a]	1.00	1.00
$-\underline{C}H_2-$	29.7	6.62	6.74	5.14
$-\underline{C}H_2-CH_3$	22.7	1.12	1.04	1.07
$-CH_3-CH_2-CH_2-(\underline{C}H_2)_n-$, n>2	29.4	1.12	0.87	0.93
$-\underline{C}H_2-CH_2-CH_3$	32.0	0.81	0.74	0.71

[a] The listed chemical shifts have the relatively strongest intensities. Other chemical shifts with weak intensities are not given.

[b] The number is obtained by taking intensity at 14.1 ppm as 1.00 and calculating intensity ratios at other chemical shifts with respect to 14.1 ppm from ^{13}C NMR.

Table 10. Experimental Matrix of Coal and Resids

H-Acceptor	Hydrogen Donor	
	Oil (hexane solubles)[b]	Asphaltene (hexane insolubles)[b]
ANT[a]	1	0
ANT	0	1
ANT	Maya resid (oil:asphaltene = 1.8:1)	
ANT	5	1
	Aromatics	Saturates
ANT	1	0
ANT	0	1
ANT	5	1
ANT	1	5
	Oil (hexane solubles)	Asphaltene (hexane insolubles)
Coal	1	0
Coal	0	1
Coal	Maya resid (oil:asphaltene = 1.8:1)	
Coal	5	1
	Aromatics	Saturates
Coal	1	0
Coal	0	1
Coal	1	5
Coal	5	1

[a] ANT = anthracene.
[b] Loading: the ratio of anthracene or coal to the sum of oil and asphaltene or the sum of aromatics and saturates is 1:2.

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