

EXPERIMENTAL EVIDENCE FOR CATALYST ACTIVITY OF COAL MINERALS

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I. INTRODUCTION

In the P&M Solvent Refined Coal Process, coal is dissolved in a coal-derived solvent to produce a filterable liquid. This is accomplished by means of a mild liquid phase hydrogenation of the coal. Filterable solutions can be made by reacting about 1.0% to 1.5% by weight of hydrogen based on the moisture-ash-free (MAF) coal. The liquid is separated from the insoluble minerals and unreacted organic matter by filtration. The solvent is recovered for recycle by vacuum flashing and the residue product is recovered⁽¹⁾.

Sufficient solvent range liquid must be made from the coal to replace any mechanical losses and those losses due to formation of gas and low boiling liquids by further reaction of the solvent. When the hydrogenation is adequate, 85% to 95% of the MAF organic matter in the coal is reacted. In typical experiments, about 60% to 70% of the organic matter in coal can be recovered as a substantially ash-free residue from the vacuum flash operation. From 5% to 10% of the MAF coal will be distilled as liquid boiling in the solvent range. Some hydrocarbon gas, water, hydrogen sulfide, and liquids boiling below the solvent range account for the remainder of the reacted organic matter. The overall conversion of organic matter and the distribution of products which is formed can be altered by changing the operating conditions. When conditions favor increased hydrogenation, the yield of liquid products is increased with a simultaneous reduction in the amount of vacuum flash residue.

It is a matter of experience that these reactions can be run with many coals without the addition of catalytic agents. This paper reports some experiments which have been done to demonstrate the nature of the catalytic effects which can be attributed to mineral phases normally present in coals. These experiments treat hydrogenation by the use of hydrogen gas⁽⁵⁾ and also by means of carbon monoxide and water as described by H. Appell and I. Wender⁽²⁾. Part of the work was done by P&M and part by University of North Dakota staff in the Chemical Engineering Laboratories of the University of North Dakota. All of the work was supported by the U. S. Office of Coal Research as part of the development of the Solvent Refined Coal Process.

II. EXPERIMENTAL

A. SOLVENT

The solvent used in these experiments is the middle fraction obtained by redistilling anthracene oil under vacuum. The fraction in question boils between 100°C. and 230°C. at a pressure less than 3 mm of mercury. The distillation is done to standardize the material and facilitate studies of yield and conversion when coal is dissolved. Normally a filtrate will contain lower and higher boiling materials than the original solvent. These are presumed to be derived from the coal or to be due to further reaction of the solvent.

Anthracene oil is a complex mixture of aromatic hydrocarbons obtained by distilling coal tar. It may contain indenenes, naphthalenes, acenaphthalenes, fluorenes, anthracenes, phenanthrenes, and pyrenes. Sulfur, nitrogen, and oxygen containing substances are also present. These elements may be substituted on the rings as -OH, -SH, or -NH₂, for example, or may be heteroatoms within the cyclic structures. Carbazole is a typical compound of this type. The molecular weights of the compounds in anthracene oil range from about 150 to about 400 with a mean value of about 200. A useful collection of spectra has been published by Karr and others which treats many compounds of this type⁽¹⁴⁾.

Many of the aromatic structures present have the ability to react with hydrogen to form hydroaromatic derivatives. Under the influence of heat these hydroaromatic substances can transfer hydrogen to other molecules and the hydroaromatic material reverts to the aromatic form.

It is therefore practical to use the composition changes in this solvent to measure certain hydrogenation effects in coal solutions. The total hydrogen content of solvent samples can be measured by combustion analysis. These results have also been correlated with infrared studies of anthracene oil and solvent reclaimed from coal solutions. It is now practical to make quite precise estimates of hydrogen content by means of these infrared correlations. Changes of hydrogen content of 0.01% to 0.02% can be measured with confidence by this means. Since the infrared method has been used to evaluate many of the experimental results discussed in this paper, the calibration data and the combustion methods required to develop the working curves will be discussed in some detail.

B. COMBUSTION ANALYSIS OF SOLVENT

The apparatus used for carbon and hydrogen determination follows the recommendations of ASTM D 271 with a few modifications designed to favor increased precision and accuracy in routine analysis⁽³⁾. This is done by using 300 to 500 milligram samples instead of the 200 milligram samples specified in the ASTM method.

C. SOLVENT AND RECLAIM SOLVENT ANALYSIS BY INFRARED

It has been observed that the relative intensity of the absorbance at 3.28 microns compared to the absorbance at 3.41 microns changes as anthracene oil is hydrogenated. Raw anthracene oil, as received, tends to be lean in hydrogen while the solvent reclaimed from coal solutions made with raw anthracene oil tends to contain more hydrogen. When anthracene oil is catalytically hydrogenated, the ratio of the 3.28/3.41 micron absorbances decreases due to a considerable increase in the intensity of the 3.41 micron band and a small decrease in the 3.28 band.

As experience and samples run under various conditions accumulated, it became possible to observe this ratio over a considerable range of hydrogen content. Representative samples were run on the Perkin Elmer 237 grating spectrophotometer at slow speed. Using the general techniques of infrared quantitative analysis as presented in ASTM E-168, a baseline was drawn from the vicinity of 2.8 microns to the vicinity of 4.5 microns. The absorbance at 3.28 and at 3.41 microns was measured and the ratio of Absorbance @ 3.28/Absorbance @ 3.41 was calculated. This

ratio will be called the IR Ratio hereafter. Precise values for total hydrogen were obtained for these samples by combustion analysis. The results were plotted on a chart as percentage hydrogen versus the IR Ratio. A line was then drawn to establish a working curve. Data for the plot are shown in Table I and the working curve is shown as Figure 1. Sample spectra showing the appearance of the 3.28 and 3.41 micron region at different percentages of hydrogen in anthracene oil are presented in Figure 2.

TABLE I

ANALYTICAL DATA - ANTHRACENE OIL AND VARIOUS RECLAIM SOLVENTS

SUBSTANCE REPORTED	% CARBON	% HYDROGEN	IR RATIO
Middle fraction of hydrogenated reclaim solvent	91.42	6.901	0.431
Run PA 39 redistilled reclaim solvent	91.38	6.616	0.674
UND 373 reclaim solvent	90.64	6.412	0.792
UND 377 reclaim solvent	90.59	6.428	0.794
UND 376 reclaim solvent	90.85	6.407	0.818
Run PA 74 reclaim solvent	90.46	6.281	1.03
UND 277 reclaim solvent	90.33	6.132	1.06
Run PA 72 reclaim solvent	90.78	6.158	1.18
Continuous Run 2 reclaim solvent	90.65	6.092	1.28
Process Development Plant Run 66 reclaim solv.	90.41	5.987	1.29
Continuous Run 8 reclaim solvent	90.93	5.925	1.33
Run PA 73 reclaim solvent	90.90	6.151	1.36
Continuous Run 11 Sample 17 reclaim solvent	91.35	6.024	1.40
UND anthracene oil redistilled at atmos. press.	90.91	5.916	1.44
Continuous Run 7 reclaim solvent	91.05	5.895	1.54
Continuous Run 12 reclaim solvent	91.20	5.896	1.64
UND 357 reclaim solvent	91.09	5.828	1.75
Middle fraction of raw anthracene oil, sample 1	91.32	5.731	1.79
Middle fraction of raw anthracene oil, sample 2	91.01	5.741	1.78

Samples shown in Table I were taken from several different sources. PA runs are P&M batch autoclave materials. UND materials are from the University of North Dakota batch autoclave runs. Continuous run samples are from P&M laboratory continuous experiments. Some materials are retained from the Process Development studies⁽⁵⁾. The original anthracene oils were from the Reilly Tar & Chemical Corp. plants at Cleveland, Ohio or Granite City, Illinois. The Granite City material is richer in carbazoles and this contributes some scatter to the data.

The IR Ratio changed from 0.43 to 1.8 while hydrogen changed from 5.73% to 6.90%. Thus, the precision of the IR Ratio corresponds to about 0.01% hydrogen. The precision of the combustion hydrogen value is about 0.03% to 0.05%. The calibration of a sensitive observation with a less sensitive one is difficult. However, the average slope established is the important information required and the number of data points available should establish this with acceptable accuracy.

It is also possible to run spectra in solution to obtain quantitative results. Anthracene oil and reclaim solvent are soluble in carbon tetrachloride and spectra can therefore be run using a solution in one cell and carbon tetrachloride in a matching cell in the reference beam. A more sophisticated differential measurement can be obtained by using the same concentration of raw solvent in the reference beam and reacted solvent in the measuring cell. In this system it is possible to relate the gain in hydrogen to a linear increase in the absorbance at 3.41 microns. Examples of this kind of data are presented in Table II.

TABLE II

DIFFERENTIAL ABSORBANCE AND HYDROGEN GAIN DATA			
SUBSTANCE REPORTED	% HYDROGEN	GAIN IN % HYDROGEN	DIFFERENTIAL ABSORBANCE
Continuous Run 14 Sample 11	5.736	-00-	Reference
Continuous Run 15 reclaim solvent	5.938	0.202	0.135
Continuous Run 11 Sample 17	6.024	0.288	0.195
UND Run 360 reclaim solvent	6.112	0.376	0.314
Continuous Run 18 Sample 7	6.148	0.413	0.298
Run PA 74 reclaim solvent	6.281	0.545	0.362
Continuous Run 19 Sample 40 reclaim solv.	6.267	0.531	0.396
UND Run 376 reclaim solvent	6.407	0.671	0.467
Run PA 39 reclaim solvent	6.616	0.880	0.670
Middle fraction of hydrogenated reclaim solvent	6.901	1.165	1.13

When these results are plotted, most of the points fall on a straight line, as presented in Figure 3. It would be reasonable to assign most of the scatter observed to the errors inherent in the measurements made. This probably is not the case for the middle fraction of hydrogenated reclaim solvent, however. This observation deviates from the trend of the other data by an amount well outside the precisions of the elemental analysis and infrared measurement. The difficulty must be qualitative. Probably the result observed is an indication that more than one kind of structure can contribute to the absorbance at 3.41 microns and that new structures are being developed in the sample. The middle fraction of reclaim solvent, in question, was catalytically hydrogenated under severe conditions which resulted in removal of sulfur, oxygen, and nitrogen as well as hydrogenation of the oil. The formation of alkyl groups during this process could probably account for the difference observed. Problems of this kind are not serious enough to keep infrared measurements from being useful in the direct observation of hydrogen transfer reactions between anthracene oil and coal.

These correlations are based on anthracene oil or anthracene oil-derived solvents which have been used and reclaimed a limited number of times. Hydrogenation conditions were mild and some sulfur, oxygen, and nitrogen remains in the solvent being recycled. The application of this kind of method to other extensively hydrogenated material has not been done.

D. CATALYSIS OF REACTION WITH HYDROGEN

A diagram of the continuous reactor system used at the Kansas City Laboratory will be found at the end of this paper as Figure 4. The dissolver tube is a piece of high pressure tubing, 1 inch O.D. x 11/16 inch I.D. and 7 feet long. An experiment was designed to study the mixing behavior of materials in the dissolver tube using anthracene oil as the solvent and coal insolubles as the tracer. It was also expected that some information about the catalytic effects of the coal insolubles could be obtained by analysis of the solvent after processing through the dissolver.

The coal insolubles were recovered from the solution made in Process Development Plant Run 66 which has been reported previously⁽⁵⁾. These insolubles had been carefully pyridine washed, followed by benzene and acetone rinses before being dried in a vacuum oven. The oven was cooled before removing the dried insolubles. Finally the insolubles were ground to pass a 100 mesh sieve before use. The ash content of this material was 46.14%. This lot of Kentucky No. 11 hvBb coal yields an ash which contains about 15% iron. Typical insolubles contain about 40% carbon and 2% hydrogen. The 5.5% total sulfur present was distributed: 0.1% pyritic sulfur, 0.5% sulfate sulfur, 1.9% organic sulfur, and 3.0% sulfide sulfur. Therefore, much of the iron is present as FeS although the presence of some oxide is not precluded. The organic material present is the most refractory carbonaceous part of the coal and has almost no tendency to react to further processing.

Experimental Procedure:

The reactor was lined out using the middle fraction of raw anthracene oil, MFRAO, as feed. This solvent was reported at the end of Table I with an average hydrogen of 5.736% and IR Ratio of 1.79. Operating conditions were: 1000 psig hydrogen, temperature 425°C., liquid space velocity 0.60/hr., gas space velocity 239/hr. The effluent liquid was sampled at half hour intervals and an infrared spectrum was run to measure the IR Ratio. At the end of 5 hours a sample was collected for a period of one hour and this sample showed an IR Ratio of 1.80 which was only a minor change when compared to the input solvent sample.

During this period, the weighed slurry feed vessel was filled with 3800 grams of MFRAO and 200 grams of washed coal insolubles. This slurry was switched into the feed loop at the end of the 6 hour line out period. Beginning immediately, samples were taken at 5 minute intervals (samples being collected for 4 minutes of each interval) for the first hour. During the second hour, samples were taken 15 minutes apart (for 5 minutes intervals). During the third hour, samples were taken 30 minutes apart (for 5 minutes intervals). Samples were taken hourly thereafter until the IR Ratio appeared to be nearly constant. Finally a sample was collected for a full hour to conclude the experiment. The slurry was pumped for a total of seven hours. All material not collected as samples was accumulated in a waste vessel. The infrared spectrum of selected samples was recorded. The samples were then analyzed for insoluble material by filtration followed by ashing the filter paper. In some cases the minerals were so fine that part of the material passed through the filter paper. In these cases the results were corrected by ashing the filtrate as well. The results were expressed as weight percent coal insolubles by using the previously determined ash content of the insoluble material.

Discussion:

The experiment generated a total of 33 samples. Eleven of these were used to line out the reactor and were only analyzed by infrared. An ash analysis was done on all of the samples made with coal-insolubles slurry feed. The infrared spectrum was run on selected samples as required to develop a smooth curve showing the change in solvent composition. The results are given in Table III.

TABLE III

DATA FOR HYDROGEN CONTENT OF EFFLUENT SOLVENT VS PERCENT INSOLUBLES					
SAMPLE NUMBER	TIME FROM SLURRY START	IR RATIO OF SAMPLE	% HYDROGEN FROM WORKING CURVE	GAIN IN % HYDROGEN	% INSOLUBLES IN EFFLUENT
11	Last Lineout	1.80	5.725	Reference	None
12	5 min.				N11
13	10 min.				N11
14	15 min.				0.001
15	20 min.				0.035
16	25 min.				0.093
17	30 min.				0.133
18	35 min.	1.79	5.733	0.008	0.234
19	40 min.				0.305
20	45 min.				0.339
21	50 min.				0.475
22	55 min.				0.614
23	60 min.				0.641
24	65 min.	1.76	5.750	0.025	0.747
25	80 min.	1.73	5.770	0.045	0.949
26	95 min.	1.69	5.790	0.065	1.19
27	110 min.	1.68	5.800	0.075	1.37
28	125 min.	1.61	5.845	0.120	1.61
29	155 min.	1.58	5.863	0.138	1.89
30	185 min.	1.56	5.875	0.150	2.19
31	245 min.	1.47	5.935	0.210	2.90
32	305 min.	1.49	5.921	0.196	2.60
33	360 to 420	1.46	5.940	0.215	3.16

Figure 5 is a graphical presentation of the course of the IR Ratio and the percent insolubles as a function of time. It can be seen that the ratio decreases as the concentration of insolubles increases. It is noteworthy that fluctuations in the concentration of insolubles also correspond to fluctuations in the IR Ratio.

Figure 6 is a graphical presentation of the gain in percentage hydrogen in the solvent as a function of the percentage of insolubles in the reactor effluent. It can be seen that the amount of hydroaromatic hydrogen, as indicated by the infrared spectrum, increased in proportion to the concentration of insolubles. Without the insolubles present the solvent showed almost no tendency for this reaction to take place under the same operating conditions.

The catalytic properties of iron are well documented in the literature^(10,11,12,13). Probably FeS is the active compound since it is the most abundant form of iron present under these conditions. This is also the form isolated at the end of the reaction. Activity has been reported for iron oxide, but considerable opportunity exists for sulfide formation by reaction with hydrogen sulfide from coal.

The insolubles fed in this experiment contained 5.5% iron. The slope of the straight line shown in Figure 6 therefore is the response due to building up a concentration of only 0.15% of iron in the effluent product. This corresponds to a rate of hydrogen addition of about 1.4% per percentage of iron in the slurry under these operating conditions. Many high sulfur bituminous coals fed in a 2:1 solvent to coal slurry will line out with 0.5% to 1.0% of iron in the slurry. The reaction rates which are observed in uncatalyzed systems are in accord with the idea that iron is the principal active agent involved.

E. CATALYSIS OF HYDROGENATION BY REACTION WITH CARBON MONOXIDE AND WATER

It has been previously reported that coal can be hydrogenated by reaction with carbon monoxide and water⁽²⁾. This reaction may be done with coal alone, or with coal slurried in a solvent. Anthracene oil is suitable for the purpose and the solutions which result have substantially the same properties observed when hydrogen is used to produce similar conversions. Appell and Wender have reported alkali metal carbonates as catalysts and have mentioned the alkaline ash content of lignite⁽⁶⁾. Increased conversion with increased sodium content has been demonstrated by York who also comments on iron oxide as a catalyst⁽⁷⁾. None of the results given are very detailed and further studies were therefore done to define the requirements for catalysis of the carbon monoxide-water reagent system more clearly.

These studies involved a program of chemical analysis and autoclave studies which were conducted as a cooperative effort by P&M and University of North Dakota workers. An excellent series of lignite samples with varying sodium content was provided by the Grand Forks Station of the Bureau of Mines. These were sub-sampled to provide both groups with comparable materials.

Preliminary work established that substantially all of the sodium, reported by the Bureau of Mines ash analysis for these samples, could be extracted by exchange with 0.01 molar calcium chloride solution. To accomplish this exchange a 6.000 gram sample of the lignite was stirred with 125 ml. of the 0.01 molar calcium chloride solution, which was then filtered into a 200 ml. volumetric flask. The material in the filter was then rinsed with additional calcium chloride solution until the flask was filled to the mark. The sodium content of the filtrate was determined by means of the Technicon AutoAnalyzer flame photo-

meter system using lithium as the internal standard. The manifold was essentially that recommended by Ussary and Gehrke for fertilizer analysis⁽⁸⁾. Further work showed that residual chloride in the exchanged lignite could be reduced to trace levels by careful washing with distilled water.

Seven lignite samples were available for these studies. These were coded UND samples 71-1 through 71-7. Some of these have been reported in Bureau of Mines literature while others have been reported only informally by means of analytical report sheets. The data and available cross reference numbers will be found in Table IV. In most cases, the sodium analysis by the extraction method checked total sodium as calculated from the ash and proximate analysis. A difference was noted in the case of the 71-1 sample which was traced to a lower ash content combined with a slightly higher water content in this subsample. Since this sample had already been used in a number of different experiments, it was necessary to use corrected values for the sodium and iron content of this sample.

The UND workers also prepared a calcium exchanged and a hydrochloric acid washed sample of the 71-1 lignite. Both were carefully washed with distilled water and dried to about the original moisture content. A detailed comparison of the 71-1 sample, the calcium exchanged sample, and the hydrochloric acid washed sample will be found in Table V.

TABLE V
COMPOSITION OF TREATED 71-1 LIGNITE SAMPLES

ANALYSIS	AS RECEIVED	CALCIUM EXCHANGED	HCl WASHED
% Moisture in lignite	32.94	29.73	30.98
% Ash in lignite	6.63	6.058	2.896
% Iron in ash	4.96	5.04	4.69
% Chloride in lignite	0.0058	0.091	0.024
% Total sodium in lignite	0.686	0.019	0.017
% Sodium in ash	10.35	0.3	0.6

The results of the calcium exchange experiments together with the HCl wash experiment suggest some rules which may be applicable to lignites in general. It appears likely that most of the sodium is in the material as a counter ion to polymeric acids which make up a considerable part of the functional groups in lignite. Calcium can be readily added by exposing the lignite to calcium ion and can be readily removed by acid washing the lignite. Part of the iron is removed by HCl washing. This observation suggests that iron and perhaps other elements may also serve as counter ions to acidic functions. Residual iron after the HCl wash is probably present as pyrite. The location of potassium and magnesium has not been studied. Ion exchange properties have been reported in recent lignite symposia^(15,16).

Experimental Procedures:

A one gallon batch autoclave was used to conduct a number of experiments designed to study the catalytic effects involved in the solution of lignite using carbon monoxide and water as hydrogenation reagents. This apparatus has been previously described⁽⁹⁾. In these experiments charges of lignite, solvent, and water were adjusted so that weights of MAF lignite, solvent, and water were the same from

TABLE IV

BUREAU OF MINES DATA - PROXIMATE, ULTIMATE, AND ASH ANALYSIS OF LIGNITE SAMPLES

UND SAMPLE NO.	71-1	71-2	71-3	71-4	71-5	71-6	71-7
Mine	Baukol- Noonan	Beulah	Baukol- Noonan	Velva Ward	Knife River Mercer	Savage	Savage
County							
State	N. D.	N. D.	N. D.	N. D.	N. D.	Mont.	Mont.
B. of M. Designation	BN 4	B-STD	BN 2	V 5	BHL	S-1	S-2
B. of M. Sample No.	GF71- 476		GF67- 685	GF70- 652	GF70- 1289		
<u>Proximate Analysis</u>							
Moisture	28.46	30	27.95	28.33	28.33	34	30
Volatile Matter	28.83	29.09	29.28	31.74	30.76	27.05	29.53
Fixed Carbon	34.62	33.40	36.48	34.88	33.82	31.19	30.82
Ash	8.09*	7.51	6.29	5.15	7.09	7.77	9.65
<u>Ultimate Analysis</u>							
Carbon			48.44	46.58	46.89		
Hydrogen			6.18	6.40	6.24		
Nitrogen			0.83	0.78	0.68		
Sulfur	0.36	0.72	0.35	0.40	0.85	0.67	0.56
Oxygen			37.91	40.74	38.25		
Ash	8.09*	7.51	6.29	5.15	7.09	7.77	9.65
<u>Ash Analysis</u>							
SiO ₂	27.2	20.2	16.4	18.8	16.1	21.3	35.7
Al ₂ O ₃	15.9	11.3	7.7	8.6	10.5	13.0	20.3
Fe ₂ O ₃	7.1	9.8	7.6	6.6	9.6	10.0	5.3
TiO ₂	0.3	0.4	0.2	0.4	0.2	0.3	0.6
P ₂ O ₅	0.1	0.5	0.2	0.2	0.3	0.8	0.6
CaO	16.7	21.8	18.4	32.5	23.2	22.7	16.4
MgO	4.3	8.0	4.1	8.1	7.4	9.3	7.0
Na ₂ O	13.5*	6.3	26.8	10.0	4.8	0.4	0.4
K ₂ O	0.5	0.3	0.3	0.5	0.3	0.3	0.9
SO ₃	13.4	21.4	13.1	12.6	25.2	21.9	12.8
Other	0.6	--	2.1	1.2	1.9	--	--
Ignition Loss	0.4	--	3.1	0.5	0.5	--	--
Na calculated from ash	0.809*	0.351	1.25	0.382	0.252	0.023	0.028
Na by calcium exchange	0.681	0.433	1.26	0.380	0.252	0.028	0.028

*Na analysis for 71-1 subsample was revised. Ash on this sample was 6.63% and contained 10.35% total sodium. This is 0.686% sodium in the lignite compared to the calcium exchange value of 0.681%.

trial to trial. An initial pressure of 1200 psig of carbon monoxide was used and the heating was standardized in an effort to reproduce average and peak temperature profiles throughout the two hour reaction period. Peak pressures could not be reproduced because variable amounts of carbon monoxide and water were consumed and variable amounts of gaseous reaction products were made. The results are evaluated by elemental and infrared analysis of reclaim solvent and the vacuum bottoms samples produced. Conversion and yield data were obtained.

The experiments were done with several kinds of materials. These are described in the following paragraphs to relate run numbers, materials, and procedure details.

1. UND Run 357. This was a blank run in which the autoclave was charged with 150 grams of distilled water plus 500 grams of raw anthracene oil. The reactor was pressurized with 1200 psig of carbon monoxide. The reactor was heated to 795°F. and held at temperature for two hours. (This final temperature was used to obtain some correlating data for comparison to the continuous unit operating at 425°C.)

2. UND Run 360. The conditions and charges were the same as UND Run 357 except that 1.25 grams of sodium bicarbonate were added.

3. A series of experiments was done by using the lignite samples with a range of sodium contents supplied by Bureau of Mines. These were charged to the reactor in amounts calculated to contain a constant weight of MAF lignite, solvent, and water. The solvent for all runs was the middle fraction of raw anthracene oil supplied by the Kansas City group. See Table I for duplicate analysis of this oil. Bureau of Mines ash and proximate analysis data together with the checking sodium and iron analysis where appropriate have been used to calculate the mineral phase compositions. The reactor was brought to an average temperature of 716°F. with peak temperatures of 725°F. to 730°F. Reaction temperature was maintained for 2 hours to allow comparison with other UND runs. UND Runs 378, 379, 380, 382, 387, 388, and 389 comprise the experiments in this series.

4. UND sample 71-1 was used to study the effect of added sodium bicarbonate on the reaction. These experiments are UND Runs 373, 375, and 376. One trial used potassium carbonate. This was UND Run 377. The standard operating conditions described in paragraph 3 above were used for all runs.

5. The HCl washed sample of 71-1 lignite was used as the feed lignite in an experiment. The standard charges and operating conditions used were the same as those outlined in paragraph 3 above. This was UND Run 390.

6. The calcium exchanged 71-1 lignite was used as the feed lignite in the standard experiment. This was UND Run 391.

Discussion:

Table VI presents a summary of run numbers, operating conditions, and materials used. The number of millimoles of sodium, potassium, calcium, and iron in each reactor charge is also presented. The results of infrared or elemental analysis of reclaimed solvent and vacuum distillation residues for each run are also included.

Inspection of the data disclosed that a strong correlation existed between gain in hydrogen and increased sodium in the charge. In the solvent reclaimed from the

solvent blank run (UND 357) the change in hydrogen content was hardly measurable. Adding only 1.25 grams of sodium bicarbonate to this same charge caused the solvent alone to gain a readily measurable amount of hydrogen. In the various experiments using lignites with a range of sodium contents, or where sodium bicarbonate was added, an increase in reaction correlated with an increase in sodium content. Substitution of potassium carbonate for sodium bicarbonate did not appear to make a substantial difference (Run UND 377 versus UND 373).

The effect of removing substantially all of the sodium from a lignite was investigated by the calcium exchange and the hydrochloric acid washing experiments. In both cases the lignites remained reactive although a marked reduction in reactivity was observed. The gain in hydrogen by the reclaim solvent correlates with the amount of iron in the lignite while the considerable difference in the amount of calcium in the samples does not seem to have much effect on the solvent composition (Runs UND 390 and UND 391 versus UND 378).

It was found by trial that the gain in hydrogen by the reclaimed solvent could be fitted to a smooth curve if the gain in hydrogen were plotted versus the sum of the millimoles of sodium, potassium, and iron. This plot is given as Figure 7.

After some speculation it was decided that a plot of the H/C mole ratio in the vacuum distillation residues versus the total millimoles of sodium, potassium, and iron charged would be an appropriate data treatment for this material. The curve for the vacuum distillation residues is given as Figure 8. The H/C mole ratio is not affected by the presence of variable residual amounts of ash, sulfur, oxygen, or nitrogen which might be factors in comparing materials from different lignites. The presence of ash in some residues was not thought to be particularly significant because its presence is largely due to failure to completely de-water some of the solutions before filtration. As a result of this data treatment only two points are off the curve by significant amounts. These are the materials from UND Run 382, in which the 71-3 sample was used, and UND Run 391, in which the calcium exchanged lignite was used. The solvent from these runs seems to fit the correlation curve better than does the distillation residue data. This may be due to the greater effect of distillation technique on the residues since it is difficult to bring all materials to exactly the same end point.

An alternative would be to assume that the calcium remained in contact with the lignite phase and exerted a small selective effect on the material which tended to remain in the vacuum residue. It is possible to move the calcium exchanged material data point to the line by arbitrarily assigning a relative weight of about 0.3 times the number of millimoles of calcium in each sample and adding these values to the total millimoles of sodium, potassium, and iron charged. This moves all points outward and produces some change in the curve shape. The initial points are nearly linear on such a plot.

Another aspect of the reaction can be studied by observing the composition of the gas which is vented at the end of the reaction. The original gas charge was 10.545 moles of carbon monoxide. The reaction generates hydrogen. Part of this reacts with the lignite and the solvent and part remains unreacted in the gas phase. Carbon dioxide is formed in this reaction and may also be formed by decarboxylation reactions as a result of heating the lignite. Some unreacted carbon monoxide remains. Table VII gives the data for vent gas composition as a function of the sum of sodium, potassium, and iron. A graphical presentation of

TABLE IV

DATA FOR CATALYTIC EFFECTS STUDY - LIGNITE - CARBON MONOXIDE - WATER

UND RUN NUMBER	357	360	373	375	376	377	378	379	380	382	383	387	388	389	390	391
Materials & Conditions																
Lignite Sample			71-1	71-1	71-1	71-1	71-1	71-5	71-6	71-3	71-2	71-1	71-6	71-7	71-1	71-1
Grams Charged			165	165	165	165	165	159.5	170	153.6	164.4	163.1	168.9	175.8	159.2	165.4
Grams Solvent	500	500	350	350	350	350	350	350	350	350	350	350	350	350	350	350
Grams Water Added	150	150	155	155	155	155	155	161.5	150.3	164.9	155.7	154.6	151.7	154.8	152	151.7
Peak Pressure Psig	4200	4180	4490	4110	4190	4190	4315	4380	4455	4395	4570	4550	4360	4200	4520	4580
Catalyst Added Gm.	None	None	1.25	2.50	5.00	10.0	2.05									
Kind	A	A	A	A	A	A	B								HCl	Ca
																Wash Exchange

Millimoles of Minerals In Reactor Charge

Sodium	---	14.9	79.0	108.6	168.2	49.2	49.2	17.5	1.7	83.5	25.0	49.2	1.7	2.2	1.0	1.3
Potassium	---	---	1.2	1.2	1.2	30.9	1.2	0.7	0.8	0.8	0.8	1.2	0.8	3.2	---	---
Calcium	---	---	32.5	32.5	32.5	32.5	32.5	46.8	53.4	31.7	48.0	32.5	53.4	49.3	---	70.5
Iron	---	---	9.7	9.7	9.7	9.7	9.7	13.6	16.5	9.2	15.1	9.7	16.5	11.2	4.0	9.0
Total Na+K+Fe	None	14.9	89.9	119.6	179.1	89.8	60.1	31.8	19.0	93.5	40.9	60.1	19.0	16.6	5.0	10.3

Reclaim Solvent Data

IR Ratio	1.746	1.134	0.792	0.773	0.818	0.794	0.776	0.831	0.976	0.814	0.846	0.814	0.990	1.155	1.347	1.164
H Value From IR	5.75	6.19	6.49	6.51	6.46	6.49	6.51	6.43	6.32	6.47	6.43	6.47	6.30	6.16	6.01	6.15
H by Combustion	5.82	6.11	6.412	6.562	6.407	6.427										
Gain in % H (IR)	0.02	0.46	0.76	0.78	0.73	0.76	0.78	0.70	0.59	0.74	0.70	0.74	0.57	0.43	0.28	0.42

Vacuum Residue Data

H by Combustion	---	---	6.93	6.928	6.84	6.834	6.844	6.496	6.090	6.263	6.361	7.172	6.063	6.151	5.564	6.146
C by Combustion	---	---	83.54	81.97	80.59	83.97	85.05	85.03	84.96	82.62	82.24	85.94	84.83	85.60	85.69	84.97
H/C Mole Ratio	---	---	0.985	1.007	1.012	0.969	0.970	0.910	0.854	0.903	0.922	1.006	0.852	0.836	0.773	0.862

A = NaHCO₃ B = K₂CO₃

the data is given as Figure 9.

TABLE VII

VENT GAS DATA

RUN NO.	LIGNITE SAMPLE	TOTAL Na+K+Fe	MOLES VENTED	MOLES HYDROGEN	MOLES CARBON DIOXIDE	MOLES CARBON MONOXIDE
378	71-1	60.1	11.46	3.01	4.20	4.25
379	71-5	31.8	11.04	1.53	4.03	5.47
380	71-6	19.0	9.67	1.01	2.23	6.42
382	71-3	93.5	12.74	3.78	6.15	2.80
383	71-2	40.9	13.53	2.52	4.80	6.15
387	71-1	60.1	11.96	2.40	5.00	4.35
388	71-6	19.0	10.35	0.63	2.88	6.53
389	71-7	16.6	10.06	0.275	2.40	7.38
390	71-1 HCl	5.0	10.06	0.168	1.56	8.21
391	71-1 Ca	10.3	10.16	0.222	2.03	7.85

When coal is dissolved in a solvent system of this kind, a complex product distribution is formed. As the organic matter in the coal is reacted it tends to lose oxygen and sulfur with the formation of water, carbon dioxide, and hydrogen sulfide. As the organic phase becomes hydrogenated it dissolves in the solvent and both solvent and coal derived material break down into smaller and more hydrogen rich molecules if conditions are favorable. At the temperatures which prevail, many thermal bond ruptures are produced and repolymerization may produce higher molecular weight products if the free radicals formed are not efficiently terminated. The net effect of these competing reactions can be altered by changing process conditions. The product distribution, (hydrocarbon gas, light liquids, solvent range liquids, heavy oils, vacuum distillation residue, unreacted organic matter, and minerals), must be defined in detail to obtain a complete description of the chemical changes which occur. Meaningful discussions of conversion and yield must of necessity involve much detail and tend to elude simple exposition.

One kind of experimental product can be evaluated by fairly direct and simple methods. The reaction can be run on lignite without the use of solvent and the conversion can be measured directly by observing the solubility of the reaction product in appropriate solvents. Benzene is conventional for this purpose, but it is usual that the residue from such extractions will still be further attacked by other solvents such as acetone or pyridine. Such conversion data is arbitrary in nature and the justification for use of any particular solvent depends on a correlation with some proposed separation process or potential end use application. Pyridine solubility correlates well with product solubility in hot anthracene oil. Only three of these samples have been run in the non solvent system. The results are found in Table VIII.

Again it is observed that the conversion increases as the total sodium, potassium, and iron content of the reactor charge increases. (See Runs 384 and 386.) However, the result for Run 385, using 71-3, is again low compared to the trend of other data. (See also Run 382.) The cause is unknown, but perhaps the organic matter in this lignite is more difficult to convert. The solvent phase run in contact with this lignite in Run 382 seems to have gained a normal amount of hydrogen. This kind of a problem may be an indication of the risks involved in attempting

close comparisons using different coals as source materials. The ion exchange properties of lignite should allow facile addition of controlled amounts of metallic ions to produce materials in which the organic phase would be strictly comparable. Such materials could become the basis for quite sophisticated catalysis and reaction rate studies.

TABLE VIII

NON SOLVENT RUN YIELDS

RUN NO. UND	LIGNITE SAMPLE	TOTAL MILLIMOLES Na+K+Fe	PRODUCT YIELD - PERCENT OF MAF COAL		
			Volatile Matter	Benzene Extractable	Pyridine Extractable
384	71-6	19.0	24.8	42.0	50.0
385	71-3	93.5	38.2	57.7	64.1
386	71-1	60.1	42.9	66.4	67.8

III. SUMMARY AND CONCLUSIONS

The information presented in this paper is the result of a number of exploratory experiments designed to reconfirm or amplify detail for a number of effects reported in the literature. The secondary objective has been to add techniques which may be useful in evaluating the effect of catalysts, and process variables, on the reactions of coal and associated solvent or liquid phases. For this reason some of the analytical work has been stressed.

The catalytic properties of iron, and FeS in particular, for hydrogenation of coal are established beyond question in the literature. The experiment done with the continuous reactor outlines a rather different way to show this affect and also illustrates the utility of an instrumental method which is sensitive and quite rapid. It has been established that the hydrogen transfer capacity of the anthracene oil-derived solvent changes in response to process variables. (It may gain or lose hydrogen depending on conditions.) When this material is used as a solvent for coal, the hydrogen transfer effects are important but rehydrogenation of solvent appears to depend on catalysis by the coal minerals.

The reaction of carbon monoxide and water also depends on catalysis. This reagent system failed to react with anthracene oil until sodium bicarbonate was introduced. The alkali content of lignite appears to be the main source of activity in this coal. Most lignites do contain some iron which contributes to the overall effect. Lignites contain some potassium but generally the amount is too small to be useful. The other extractable ion generally present is calcium. Its probable location as a counter ion to polymeric acid functions suggests that it may also become catalytically active as the lignite is decomposed. These experiments have not been conclusive, but a lower order of activity for calcium seems probable.

The hydrogenation effects may be followed by observing solvent or vacuum bottoms compositions. Correlating conversion data based on composition of gaseous products is also obtainable. These changes can also be shown by observation of the detailed distribution and yield of liquid and vacuum distillation products although such detail has not been presented here.

It seems probable that the ion exchange properties of lignite could be utilized to prepare carefully controlled materials for reactivity studies. These materials could be used in the autoclave or in the continuous reactor to develop quantitative relationships for the elements of interest.

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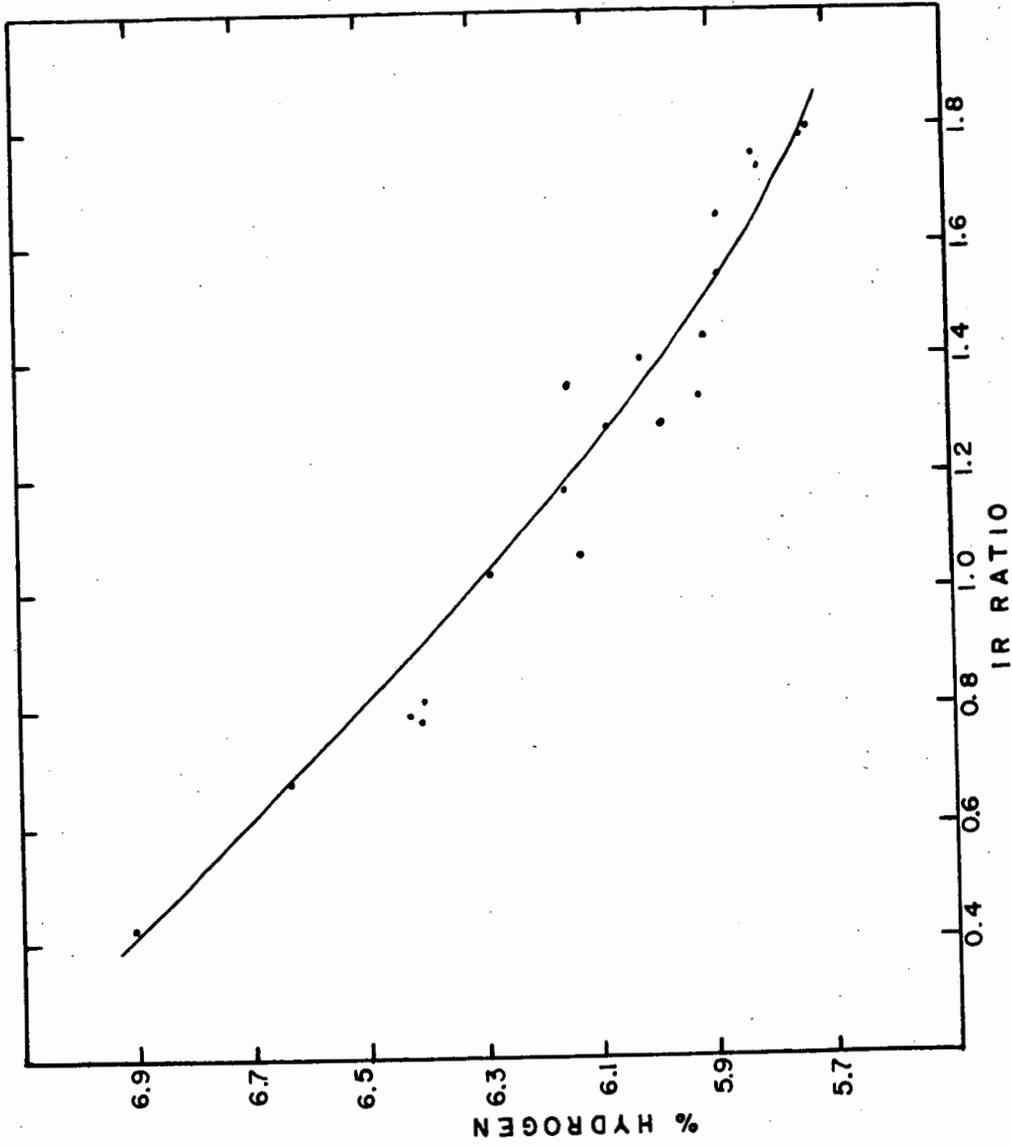
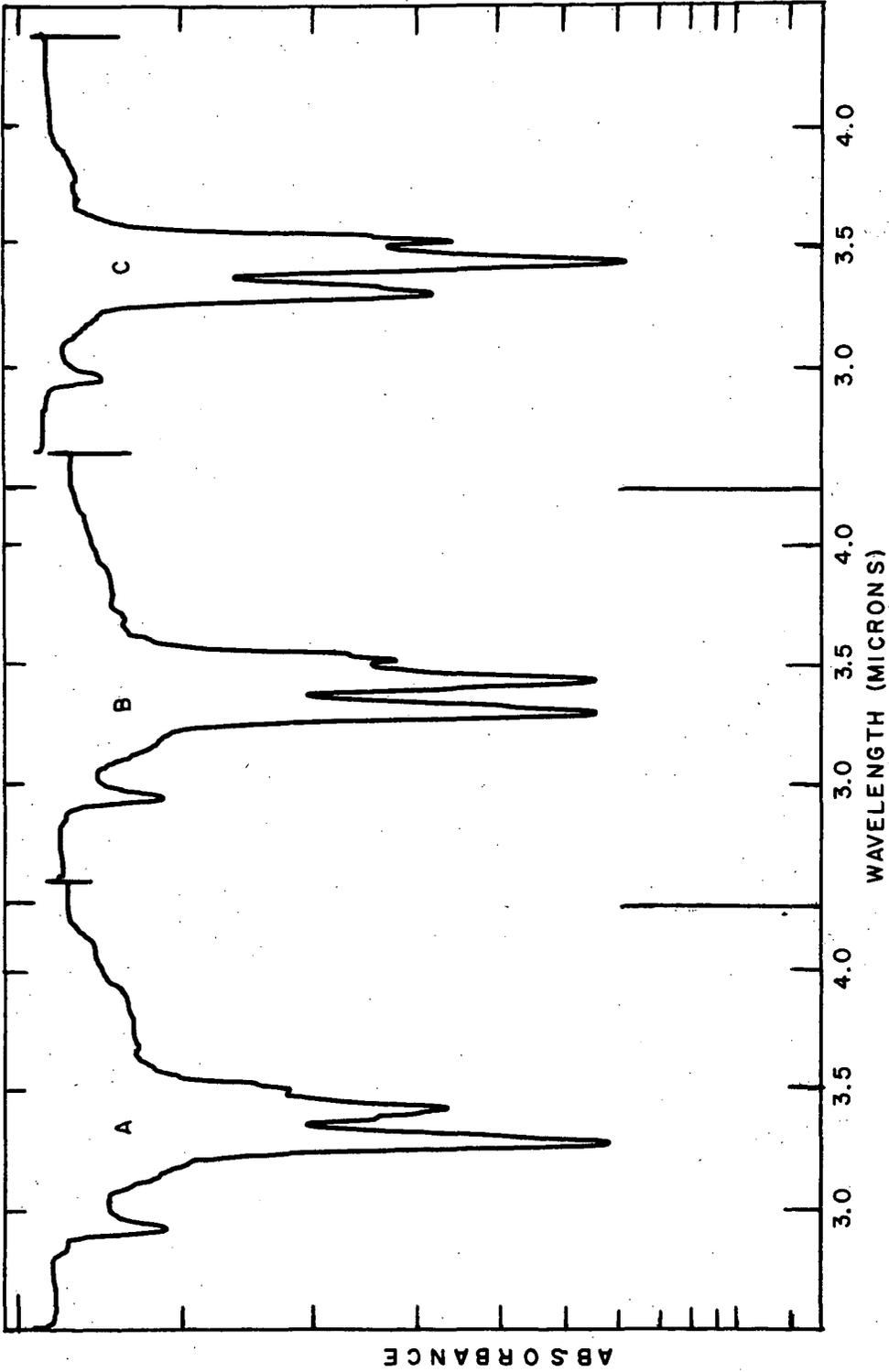


Figure 1. WORKING CURVE % H IN SOLVENT



A. MIDDLE FRACTION OF RAW ANTHRACENE OIL. B. MIDDLE FRACTION PARTLY HYDROGENATED.
C. MIDDLE FRACTION OF HYDROGENATED RECLAIM SOLVENT.

Figure 2. COMPARATIVE SPECTRA

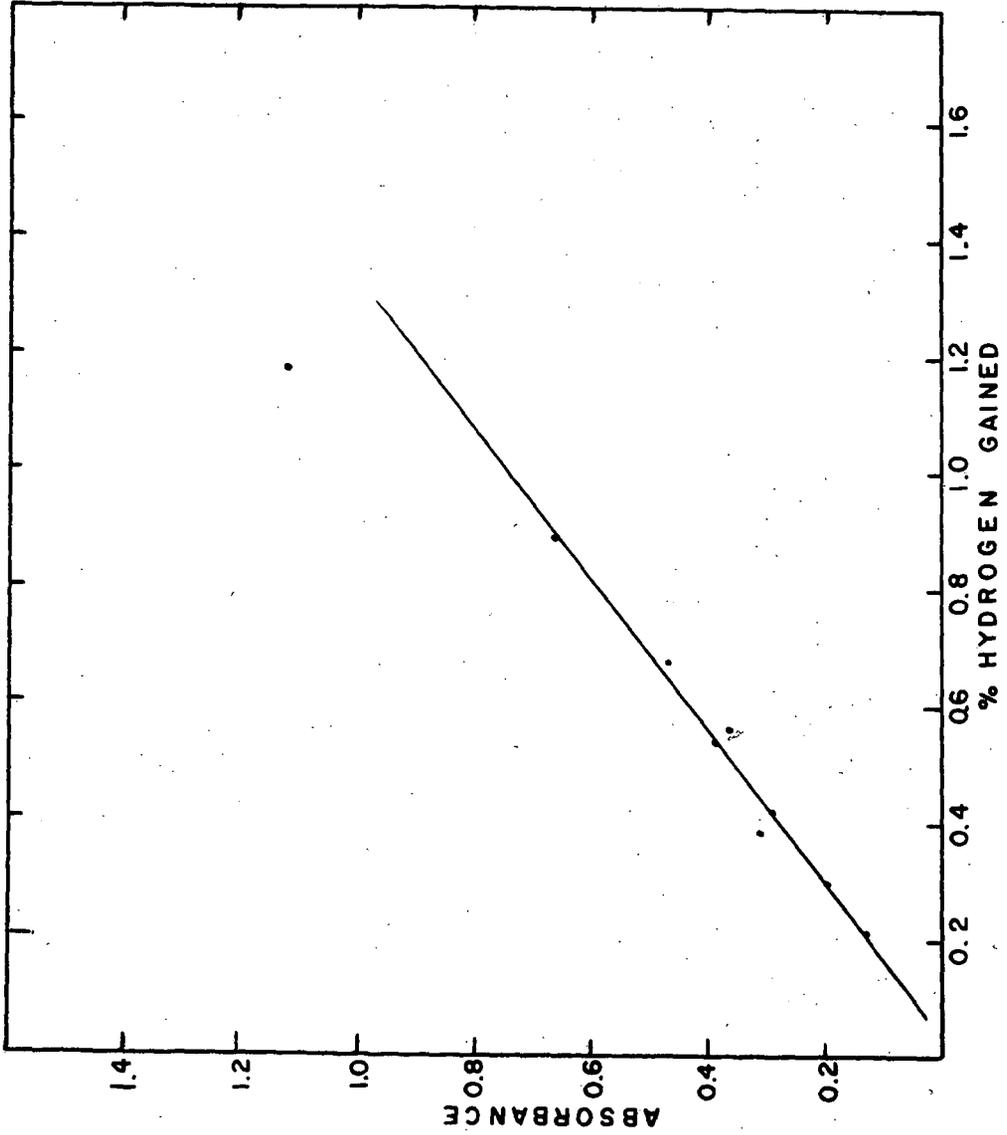


Figure 3. DIFFERENTIAL IR WORKING CURVE

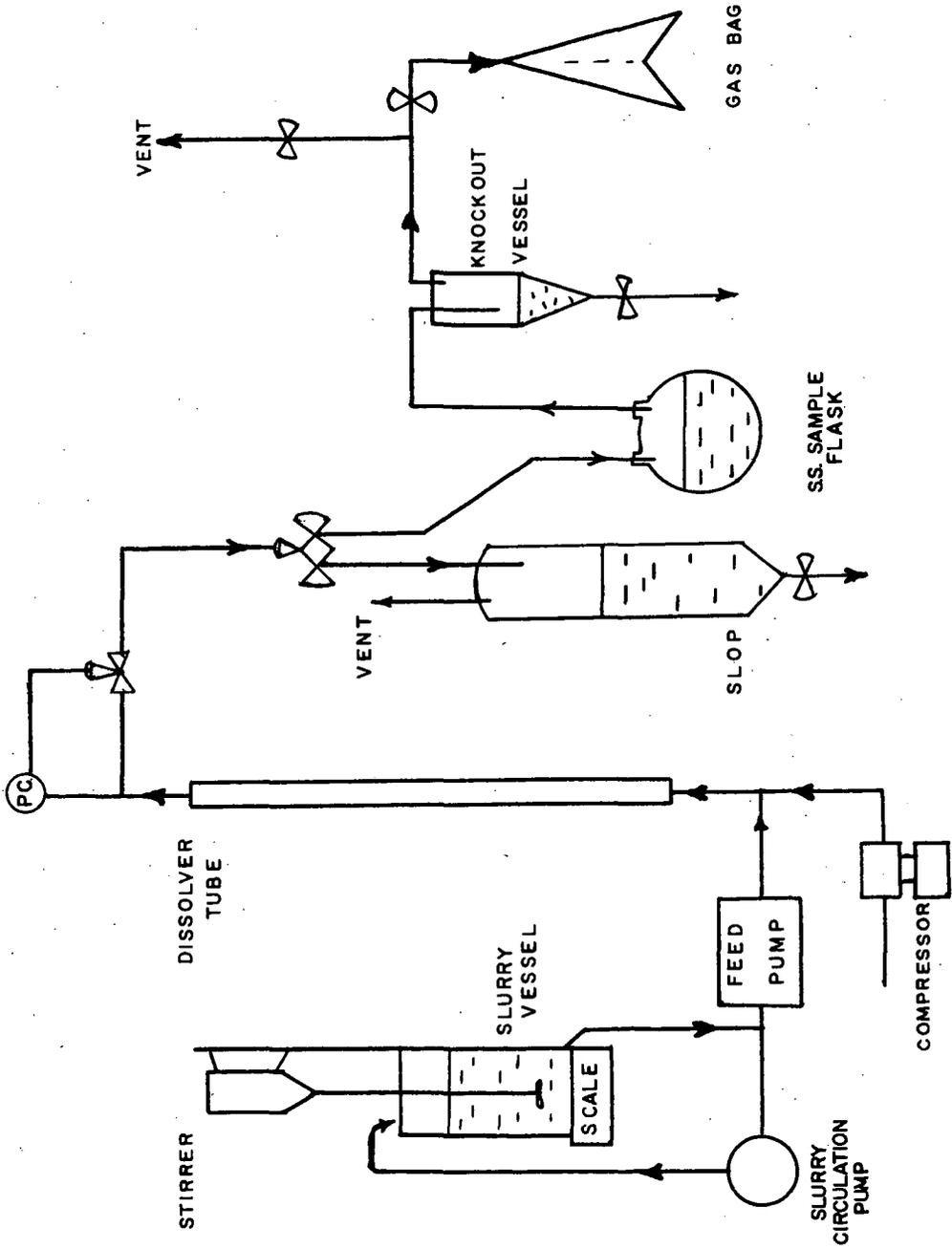


Figure 4. SIMPLIFIED FLOW DIAGRAM - CONTINUOUS DISSOLVER

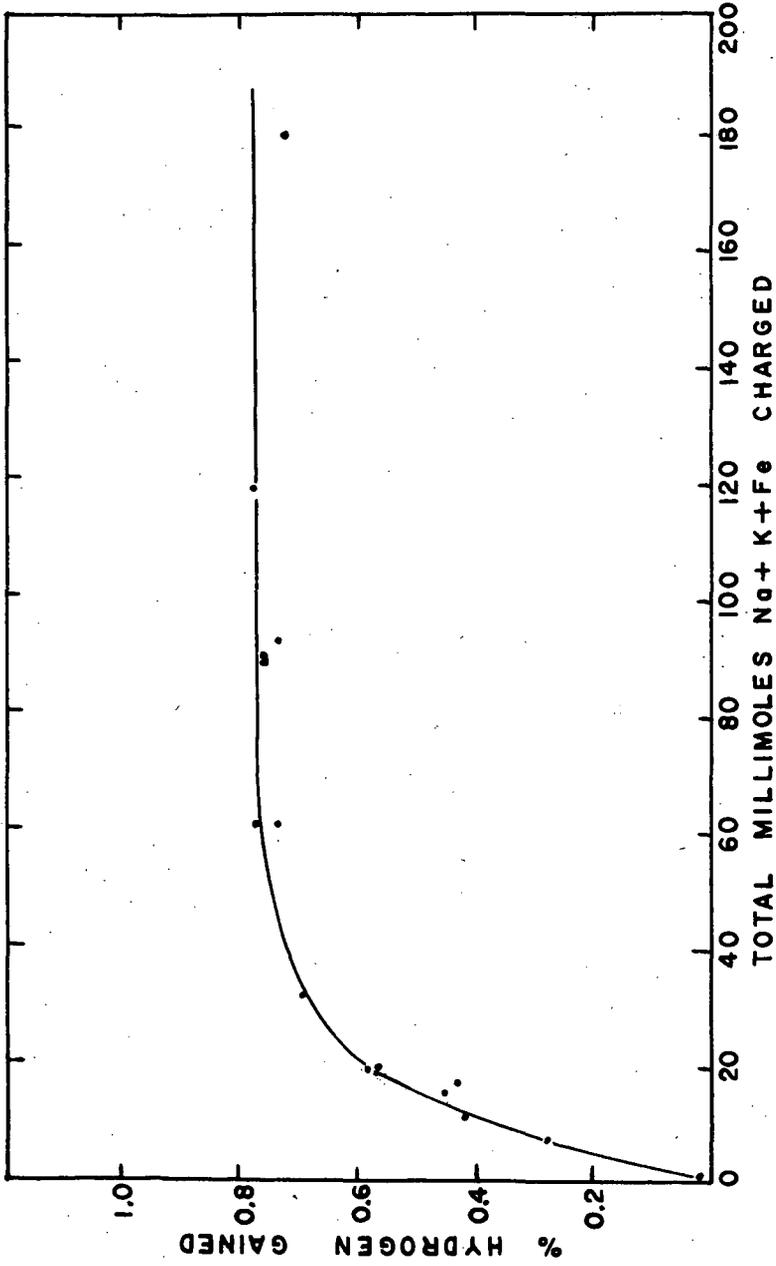


Figure 7. HYDROGEN GAINED BY RECLAIM SOLVENT

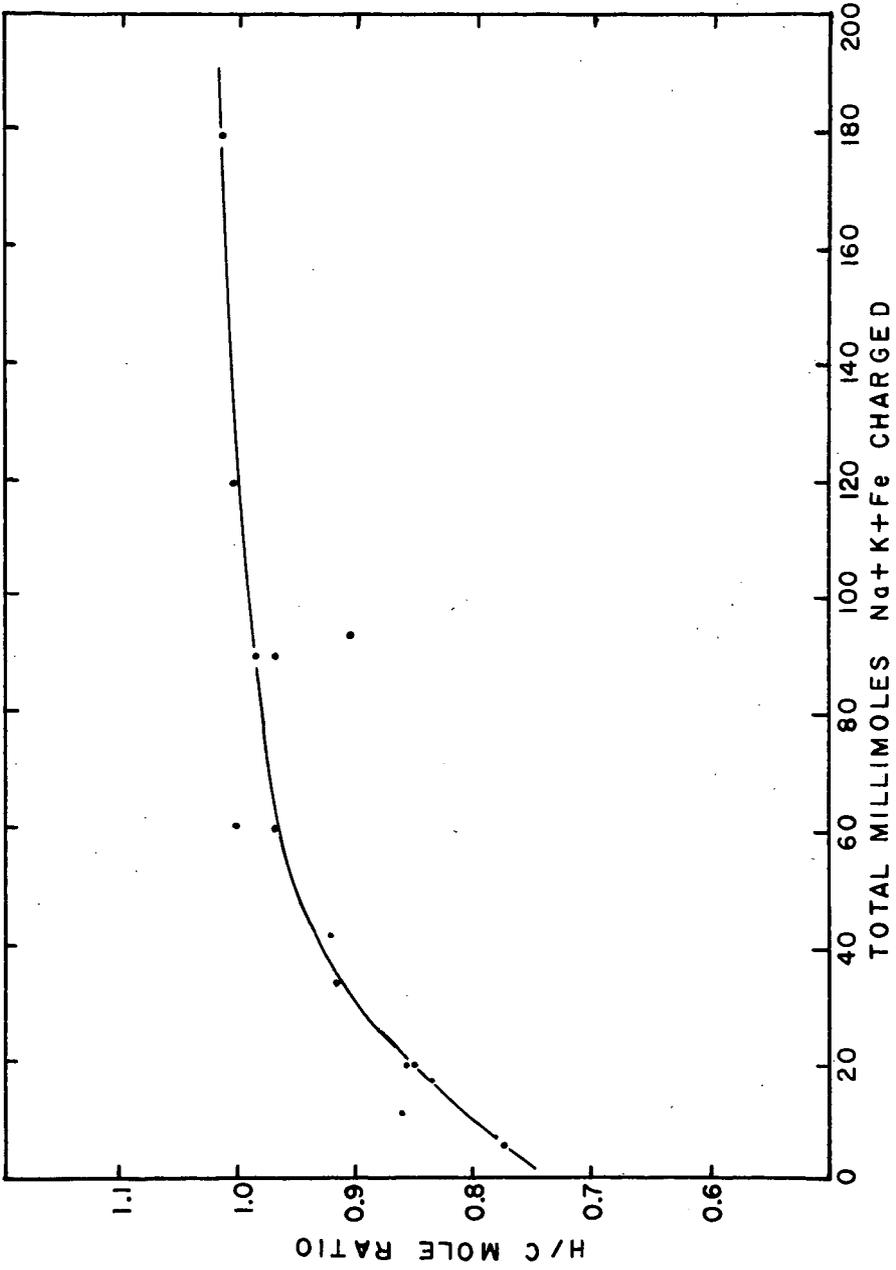


Figure 8. COMPOSITION OF VACUUM DISTILLATION RESIDUES

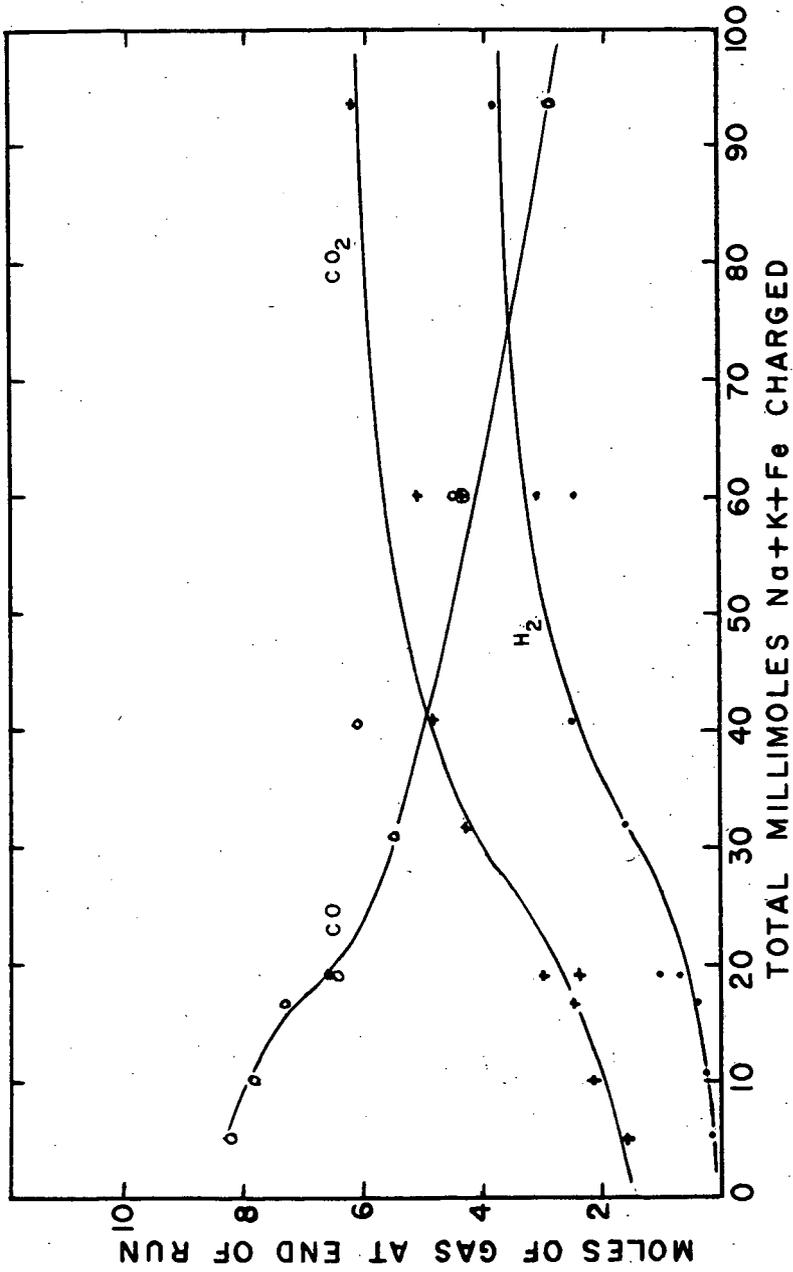


Figure 9. VENT GAS COMPOSITION AT END OF EXPERIMENT