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PROJECT WESTERN COAL: COMPILATION OF FOUR 1967 REPORTS

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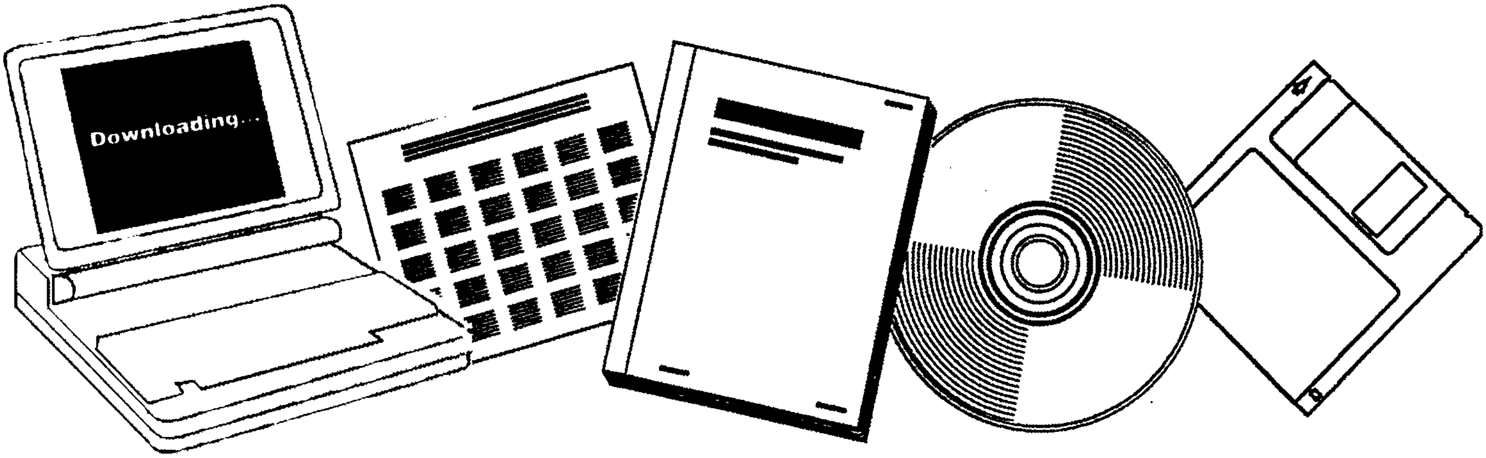

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PROJECT WESTERN COAL - 1967 INTERIM REPORTS

1. Flash Heating and Plasma Pyrolysis of Coal by L. L. Anderson, G. R. Hill, E. H. McDonald and M. J. McIntosh
2. A Kinetic Study of Coal Extraction by Tetralin with Ultrasonic Irradiation by Virginia Cheng Chen Ching, Larry L. Anderson, Wendell H. Wiser and George Richard Hill
3. A Kinetic Comparison of Coal Pyrolysis and Coal Dissolution by Wendell H. Wiser
4. Kinetics of the Hydro-Removal of Sulphur, Oxygen and Nitrogen from a Low Temperature Coal Tar by S. A. Qader, W. H. Wiser, and G. R. Hill

UNIVERSITY OF UTAH
Salt Lake City, Utah

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INTRODUCTION

The four sections of this technical report present some results of research from Project Western Coal during 1967. Project Western Coal, sponsored by the U. S. Office of Coal Research and by the State of Utah has as its objective the determination of the reaction characteristics of coals in the Western United States related to their use as potential sources of liquid and gaseous fuels and chemicals. Work on this project started in 1962 and is continuing.

Section one summarizes the results obtained as coals were heated extremely rapidly to distillation temperatures, in atmospheres of hydrogen and other reducing gases. Flash heating of fine coal by a controlled high intensity discharge from a flash tube resulted in the production from the coal of a distillate fraction rich in paraffin and iso-paraffin components in yields higher than Fischer Assay distillation yields.

The extremely high temperatures in the hydrogen arc plasma (second portion of section one) caused the coal distillate molecules to fragment into the smallest thermodynamically stable gas molecules. Here again the yields from the high volatile coals tested were higher than expected from studies on other coals.

In Section two are reported the results of the kinetic study of coal extraction by tetralin in an ultrasonic field. Prior studies in this laboratory indicated that the dissolution of coal might be accelerated if fresh surfaces were continually made available upon which the solvent could act. The results reported herein more than confirm the assumption; apparently the solubility of the coal is increased as well as the rate of solution.

Section three compares the kinetics of coal pyrolysis and coal dissolution as determined on identical samples of several western coals. The mechanisms presented correlate kinetically-for the first time-the two types of processes currently being investigated by OCR contractors for obtaining liquids from coal.

The final section in the volume presents kinetic data on the removal, by hydrogenation, of sulfur, oxygen and nitrogen atoms from the liquid fuel components in primary coal tar. The reduction in the content of non-hydrocarbon components is required if the liquids are to be used as a petroleum supplement. The kinetic data enable design engineers to predict time required for the necessary treatment at various temperatures and pressures (of hydrogen).

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FLASH HEATING AND PLASMA PYROLYSIS OF COAL

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ABSTRACT

High volatile bituminous coals from Western United States have been subjected to high energy flash heating and to hydrogen arc plasma pyrolyses. Each method of pyrolysis produces volatile products in excess of ASTM volatile matter determination due to the very high rate of energy absorption and of quenching.

The flash heating primary distillate from the coals tested is a brown solid, mainly hydrocarbon, whose IR spectrum differs markedly from the original coal. The products formed in different gaseous atmospheres are significantly different.

Due to the high temperatures in the hydrogen atom plasma, the principal carbon-containing distillate products from coal are acetylene and hydrogen cyanide.

Product yields as a function of energy input and of gas composition will be presented.

Pyrolytic Reactions of Coal

The rank of a coal depends on only one or two properties. Volatile matter (or fixed carbon) is one of the most important criteria for classification. According to the ASTM test for volatile matter the coal (or coke) is placed in a tube furnace, the temperature of which is 950 ±20°C. The heating time is seven minutes. Although such a simple and somewhat arbitrary test seems quite unscientific the results reflect the nature of the bonding in the coal and many other important properties. This study includes two rather different methods of pyrolyzing which give valuable information on the nature of coal.

Pyrolytic reactions of coal have been studied previously (1,2,3,4,5) by methods similar to those presented here. In general when high volatile coal is subjected to very rapid heating more can be volatilized than in the ASTM volatile matter determination. Some of these studies were carried out to study the gaseous products of the reaction. The composition was found to depend on the temperatures and gas phase present during the reaction. Very little effort was directed to the properties of the devolatilized solids. Some experiments have been conducted specifically for the synthesizing of certain compounds, such as metal nitrides, cyanogen, and nitrogen dioxide (6), and acetylene (7,8).

The purpose of the present studies was to obtain information from pyrolyzing of coal that can be used to increase our understanding of the basic coal structure. It has been known for some time that the coal "molecule" or basic unit is a difficult quantity to describe. The understanding of present investigators has been obtained from not only improved methods of analysis but also from information about coal reactions. Hill and Lyon (9) have suggested a structure for coal that has been obtained in this way.

In the two types of pyrolysis of this study information was obtained which indicates that coal as well as products from coal reactions contain two distinctly different fractions. A close look at the characteristics of these fractions suggests a basic conclusion regarding coal reactions and conversion of coal to more economic forms.

Apparatus and Experimental Methods

The samples used for this study were Utah high volatile bituminous and subbituminous coals. Some cursory flash heating of two West Virginia coals was also done as well as some arc plasma pyrolysis of oil shale and coke for comparison purposes.

Flash Heating Apparatus. This consisted of a power supply, a condenser bank, a photoflash tube and auxillary wiring. The apparatus was assembled in the Fuels Engineering Dept. at the University of Utah. The circuit diagram for the unit is shown in Figure 1. The power supply was used to charge the condenser bank, consisting of three 125 microfarad capacitors, to the desired voltage. The photoflash tube was a General Electric F.T 524, consisting of a quartz helical tube with an electrode sealed in each end, and a trigger electrode on the external wall. The tube was filled with xenon and the electrodes were connected across the capacitor bank. The tube was triggered by a high voltage pulse from an ignition coil and battery. The flash duration (time above one-third peak power) in the circuit used was approximately two milliseconds.

Fine coal particles (10 to 40 microns diameter) were suspended on the inner walls of pyrex tubes and exposed to flash lamp irradiation. This was done by placing the pyrex tubes inside the coils of the flashlamp after evacuating and sealing them. After flashing the coal the products in the tube were analyzed.

Plasma apparatus. This apparatus was also constructed in the laboratory. It consisted of four flow meters, a plasma jet, a sample feeder, a cooling chamber and a large collection balloon. Essential features of the plasma jet are shown in Figure 2. The power supply used was a Miller arc welder transformer (Model SRH555). The plasma torch operated continuously at 6 kw. for periods of up to more than two hours. This torch was patterened after one designed by Stokes and Knipe (6) with several modifications.

Powdered coal was fed into the plasma after the gases passed through the electrical discharge but before they had emerged from the end of the torch. The hot gases and entrained solids passed into a water cooled chamber containing baffles and a steel wool filter. The gases were collected in a large weather balloon.

Results and Significance - Flash Heating. The results of the flash heating experiments were evaluated by visual and microscopic observations, gas and proximate analyses, and extraction of products. Infrared absorption patterns of the original coal were compared with those of products of flash heating. Plasma reaction products were tested similarly. Gas compositions were determined and proximate analyses performed on solid products. Methane, oil shale, coke and activated charcoal were also run in the plasma for comparison purposes. The results of these experiments were used to interpret the results from the experiments with coal.

Flash heating results indicated that coal is composed of two distinct substances. These substances react differently when subjected to the radiant energy from the flashlamp.

In the flash heating experiments fine particles of Spring Canyon coal were suspended on the inner walls of a pyrex tube before it was evacuated and sealed. The tube then appeared transparent with a dusky grey color due to the suspended coal. Upon flashing the tube instantaneously became black and opaque. Strings of gossamer-appearing material formed inside the tube as well as a coating on the tube walls. Careful examination of the material in the tube showed that there were two distinct products present. The two products were a black material (B) and a yellow, more volatile substance (Y). B is highly aromatic, very stable thermally, difficult to oxidize, and composed of small colloidal-sized spheres, probably polymeric, approximately 350 Å in diameter. Y, unlike B, is highly saturated, unstable thermally, easily oxidized, of average molecular weight 750, and is a heavy semi-solid.

After analyzing the results of the flash heating experiments it appears that Y is mostly a product of the volatile matter in coal. Some peculiarities of the formation of Y are as follows:

> When coal is flashed at 1500 volts in a vacuum or a non-oxidizing atmosphere, Y will apparently form to a considerable extent with not much formation of B.
>
> If the products of flash heating are flashed several times at successively higher voltages the yellow color becomes darker and above 1900 volts the products are black and opaque.
>
> If coal is flashed with oxygen in the tube containing the coal no trace of Y is found.

The extent of the formation of B by flash heating depends somewhat on the voltage discharged through the flash tube. However, B will form in oxygen or any other atmosphere used.

Description of Products -- Flash Heating   Several methods were used in the examination of B, Y and Spring Canyon coal in an effort to determine their properties and the types of reactions taking place during the flashing of the coal.

I. Volatile Matter and Coking Test.

The volatile matter content for B obtained by flashing coal at two different voltages is compared with the volatile matter in the original coal in Table 1. The values were obtained by using the standard ASTM procedure for volatile determination. In the test the coal coked to a much harder coke than the B formed at 1500 volts. The B formed at 3000 volts did not coke at all.

TABLE 1

ASTM VOLATILE MATTER TEST DATA ON B AND COAL

	B formed at 3000 volts	B formed at 1500 volts	Spring Canyon Coal
Initial weight	0.424 gm	0.045 gm	1.459 gm
Weight volatilized	0.079 gm	0.253 gm	0.650 gm
Percent volatile matter	18.6	39.2	44.5

II. Infa Red Spectra

Spectra for coal, Y, and B are given in Figures 4,5,6,7. The spectra were obtained for samples pressed in KBr. Only micro amounts of sample can be used in the KBr to yield a disc suitable for analysis. Therefore, quantitative results were deemed impractical by the method employed.

The most valuable information obtained from the spectra was from peaks observed at 3030 cm^{-1} due to aromatic C-H stretching and just below 3000 cm^{-1} arising from aliphatic C-H stretching. The C-H stretching intensities can be used to obtain H_a/H_s (aromatic to aliphatic hydrogen) ratios. If we assume a Beers Law extinction coefficient of 0.5 after Brown (10) the following values are obtained:

		H_a/H_s
Spring Canyon Coal		1.132
BCR coal No. 1031		1.51
BCR coal No. 1007		1.54
B samples	ca.	1.70
Y washed with benzene only		0.106
Y washed with acetone only		0.077
Y washed with acetone 1st benzene 2nd		0.186
Y washed with acetone 2nd benzene 1st		0.099

Examination of the spectra show that there are no significant differences between the coal spectra and spectra for B except for the differences in H_a/H_s values. However, the spectra for Y are all different in many respects from those of coal and B. Furthermore there are significant differences in the Y spectra from the benzene and acetone extracts. This indicates that Y is a mixture of different substances. The spectra for Y are shown in Figure 6.

To determine more about the chemical nature of Y spectra were compared for Y, benzene solubles from coal (extracted with cold benzene), benzene solubles from a low temperature (400-800°C) coal tar, and a clear colored oil which appeared to separate from Y after solvent was evapprated at 100°C. Examination of the spectra showed all of these substance to be different with the material from L.T. tar and coal having much sharper and more distinct aromatic C-H stretching peaks. The significance of this and other information regarding the structure of Y will be discussed in a later section.

III. Microscopic and Miscellaneous Measurements.

B was fractionated by density, 95% being in the range 1.35 to 1.525. No trends of particle size or composition with density were found. Various density fractions of B were also tested for ash content and heat of combustion but no trends with density were observed.

When coal was flashed at 3500 volts in a tube a thin film of B was deposited on the tube wall. The film exhibited an interference color (yellow). Assuming first order reflection the thickness of the film was calculated using a method developed by McAdam and Geil (11). In this method the thickness is calculated by

$$\text{film thickness} = \frac{(2b-1)}{4\mu} \lambda$$

where μ = refractive index of the film, λ = wavelength of light reflected, and b = order of reflection. For first order yellow λ was taken as 2209 angstroms; the refractive index for coal was used, $\mu = 1.75$. The film thickness by this calculation was 316 angstroms. Microscopic examination showed that the particle size of B was in this same range indicating that the yellow film was made up of a single layer of B particles approximately 300-350 Å in diameter.

The results of flash heating are summarized as follows:

The benzene-soluble portion of Y was tested by osmometry and an average molecular weight of 750 was determined.

The density of B was approximately 1.43.

Particle diameters for B were 300-350 Å.

Essentially all of the ash in the coal was found in B.

When coal is reacted to produce B and Y if these are separated B will not coke. When coal is flashed at low energies (So that all of the Y is not reacted) some coking property is retained by the B produced.

Results and Significance - Plasma Pyrolysis

Plasma temperatures were calculated for the different gas mixtures before coal was added. The following assumptions were made in the calculation of the plasma temperature:

1. The change in enthalpy of the plasma gases was equal to the difference between the input energy and the heat loss to the cooling water.
2. The plasma was in thermal equilibrium.
3. The important species present were; argon, molecular

hydrogen and nitrogen, and atomic hydrogen and nitrogen.

4. The important equilibria were

$$H_2 = 2H \text{ and } N_2 = 2N$$

5. Because of the small values for the equilibrium constants, reactions between nitrogen and hydrogen were neglected.
6. There were no ionization reactions.

The last assumption was not exactly true because the plasma flame was bent slightly by a magnetic field. However, thermodynamic data indicated that ionization was negligible.

The plasma contained heat in two forms; the sensible heat of each of the species and the heat of dissociation of the molecular species. The sensible heat of each component was the product of n, its number of moles, C_p its mean molar heat capacity, and the temperature change. The amount of dissociation of hydrogen and nitrogen was calculated from the equilibrium constants involved, and so the energy used in dissociation was readily found.

The heat content was given by the following equation:

$$\Delta H(\text{calories}) = (n_H\ C_{p_H} + n_{H_2}\ ,C_{p_{H_2}} + n_N\ C_{p_N} + n_{H_2} + C_{p_{H_2}} + n_A\ C_{p_A})$$

$$\Delta T + n_H\ 52{,}000 + n_N\ 85{,}000.$$

It was necessary to solve this equation by trial and error. A value for ΔT was chosen, and the concentrations of all the species present were calculated using the equilibrium constants for ΔT + 300°K. These concentrations along with the proper mean C_p values were then used to calculate a value of ΔH. When the calculated enthalpy change agreed with the measured change, the plasma temperature was determined. A computer program was developed to facilitate these calculations.

Product yields were recorded as percent of total weight of coal, and as percent of the volatile matter distilled from the coal that was converted to products.

Two different ranks of western coals were used in these experiments, a high volatile coal from Spring Canyon, Utah, and a subbituminous coal from Coalville, Utah. The high volatile coal had the following analysis: volatile matter 49.3 percent, fixed carbon 45.4 percent, moisture 1.4 percent, carbon 73.4 percent, hydrogen 5.9 percent, nitrogen 1.1 percent, oxygen 13.6 percent, sulfur 0.6 percent, and ash 5.3 percent. The proximate analysis of the subbituminous coal was 50.0 percent volatile matter, 45.7 percent fixed carbon, 5.5 percent moisture, and 4.3 percent ash. The ultimate analysis was calculated by a method discussed by Smith and Stinson (1[illegible]). The values thus calculated for the subbituminous coal were: carbon 70.5 percent, nitrogen 1.6 percent, hydrogen 5.5 percent, oxygen 18.2 percent, and ash 4.3 percent.

For comparison purposes, oil shale, methane, coke from the high volatile coal were also used as samples.

The different gas compositions and flow rates used were: pure argon flowing at 15 liters per minute; a mixture of 12.3 percent hydrogen in argon flowing at 17.1 liters per minute; a mixture of 20.0 percent nitrogen in argon flowing at 18.7 liters per minute; and a mixture of 18.0 percent nitrogen and 10.0 percent hydrogen in argon flowing at 20.8 liters per minute. These four gas compositions and flow rates were chosen because they gave a stable arc and a high concentration of hydrogen and nitrogen for reaction purposes.

The high volatile coal was difficult to feed continuously because of its coking properties. A layer of coke gradually built up around the sample feed opening in the plasma jet nozzle and eventually plugged the hole entirely. The subbituminous coal was noncoking, and so there was no problem with plugging. The average fluctuation in the sample flow from the mean value was about 26 percent for both coals.

All samples were ground small enough to pass a 200 mesh screen. After a sample had passed through the plasma jet, it was again sieved, and an A.S.T.M. volatile matter determination was done on the residue which passed a 200 mesh screen.

Some of the reactions were quenched with a water spray about three centimeters from the plasms jet nozzle. In these experiments, the coal was recovered from the quench - water by filtration, dried over night at 110°C, sieved and the volatile matter determined.

The experiments are grouped in Table I through VII according to plasma composition. All "a" runs were pure argon plasmas, "b" runs were argon - hydrogen plasmas, "c" runs were argon - nitrogen plasmas, and "d" runs were argon - hydrogen - nitrogen plasmas. A capital letter in the run number indicates that the experiment was water-quenched. The following abbreviations were used in designating the sample used: hv - high volatile coal, sub - subbituminous coal.

There was a wide variation in the data that was obtained, but there were some general trends that developed. Acetylene production doubled when the plasma gas was changed from pure argon to a mixture containing 12 percent hydrogen. This effect was true for both the high volatile and the subbituminous coals, and for the quenched reactions as well as the nonquenched ones. This was in agreement with the work of R.L. Bond <u>et. al</u>.(4). They found that acetylene production from coal doubled when a 10 percent hydrogen mixture was used instead of pure argon.

The use of a plasma containing 20 percent nitrogen in argon gave the same acetylene production as a pure argon plasma, but the production of hydrogen cyanide was increased by about five times in the nonquenched reactions. The quenched reactions were low in hydrogen cyanide, and in some cases none was found. It was thought that the water spray was taking the HCN out of the gas phase, but a qualitative test of the quench water for cyanide ion was negative.

The hydrogen - nitrogen - argon plasma gave products that were essentially the same as those obtained from the nitrogen - argon plasma; i.e. the additional hydrogen had no effect. This was rather surprising when the addition of hydrogen caused such a large increase in acetylene production as compared to pure argon. Equilibrium calculations showed that less than 0.10 percent of the hydrogen was tied up in nitrogen - hydrogen compounds, and so there was still a relatively high concentration of hydrogen atom present.

The high volatile coal gave higher yields of methane, acetylene, and hydrogen cyanide than the subbituminous coal. This was true for all of the different plasma compositions and for the quenched and nonquenched reactions. The carbon monoxide and carbon dioxide yields were generally greater for the subbituminous coal. No trend appeared for the hydrogen yields from the two different coals.

The difference in the products appeared to be related either to the moisture content or the chemically combined oxygen of the two coals. The subbituminous coal had five times as much moisture as did the high volatile coal. The oxygen for the increased carbon dioxide and carbon monoxide could have come from the water. This would have produced higher hydrogen yields, and since this was not the case, the difference in moisture contents did not appear to account for the product differences satisfactorily.

The subbituminous coal had about five percent more chemically combined oxygen than the high volatile coal. If this oxygen were used to produce the extra carbon oxides and some water there would have been a decrease in the acetylene and hydrogen cyanide and no change in the hydrogen gas production as compared to the high volatile coal. The production of actelyene and HCN dropped because carbon and hydrogen that would have been available were tied up with the oxygen. Perhaps a few experiments with known oxygenated compounds would help to define the nature of the oxygen in coal. One would expect heterocylic and straight chain ether linkage to react differently then ketone, aldehyde, ketal or acid groups.

Methane, oil shale, activated charcoal, and coke samples were run for comparison purposes. Methane conversion to acetylene was about the same as for the conversion of the total coal. It was expected that the methane conversion would have been much greater. One reason for the low conversion may have been the high sample feed rate. Heating over a mole of methane per minute probably reduced the temperature enough to lower the conversion. Oil shale did not produce as much acetylene and hydrogen cyanide as did coal. But here again, the sample feed rate was very high, and so a much cooler reaction would have resulted. A large part of the shale was an inorganic material that fused when it passed through the plasms plane and thus caused further cooling.

Activated charcoal and coke samples were unreactive except in the water quenched reactions. Carbon monoxide, carbon dioxide, and hydrogen were produced in the presence of the water spray.

Since coke and charcoal samples produced only traces of acetylene, it was assumed that only the volatile matter in the coal was reacting to give products. This is in agreement with the results of the flash heating results. Since the volatile matter seems to be the reactant in the coal the distilled volatile matter was used as a base for comparing product yields.

Several runs were made using some catalysts. Cobalt molybdate and zinc chloride were selected because they have been used with good success as coal hydrogenation catalysts. Calcium chloride was also used to see if calcium carbide would be easier to form than acetylene. The samples were all approximately two-thirds coal and one-third catalyst.

Zinc chloride and cobalt molybdate reduced the production of acetylene and hydrogen cyanide by as much as 50 percent for argon-hydrogen plasmas. In an argon-hydrogen plasma the calcium chloride caused a reduction of only about 10 percent. However, in an argon-nitrogen plasma, the addition of calcium chloride was accompanied by an increase in the yields of hydrogen, methane, acetylene, and hydrogen cyanide. Carbon monoxide and carbon dioxide were absent. No calcium carbide, chlorine gas, or chlorine compound were found in the reaction products. Since calcium and chlorine ions were present in the plasma, it was unlikely that the formation of the products goes through an ionic mechanism. Generally, the addition of catalytic material in large quantities was detrimental to the formation of products. However the magnitude of the reduction was not the same for all compounds.

Quenching the reactions with a water spray had little effect on the amount of distilled volatile matter that was converted to acetylene. However, the amount of volatile matter driven off was much less than in the nonquenched runs. The weight of the carbon and hydrogen in the products of the water quenched reactions was greater than the weight of the distilled volatile matter. This difference was accounted for in the large increase in hydrogen gas, carbon monoxide, and carbon dioxide. These products were also formed when coke was water-quenched. They were formed by the interaction of incandescent coal or coke particles and water in the familar water gas reaction. The entire particle was able to react, and so yields greater than the distilled volatile matter were possible.

Some of the quenched reactions produced nitric oxide. The runs where nitrogen was used in the plasma gases produced as much as 0.5 percent nitric oxide on a total volume basis. Small quanities of NO were produced in two of the subbituminous coal runs where no nitrogen was used. It was assumed that the nitrogen came from air, but possibly it came from the coal itself.

The amount of volatile matter driven out of the coal was dependent on the temperature and the sample feed rate. The sample feed rate had a greater effect than the temperature. In conjunction with this, the highest conversions were generally for the lowest sample feed rates. The temperature effect on conversion showed no clear trend. Other factors overshadowed any change which temperature variation might have caused. This was not too surprising since plasma temperatures were a lot higher than 2000° K. which was the most favorable temperature for the reactions.

X-ray examination of the coal and coke showed a change in the graphite or graphite-like material. The x-ray peak for the graphite 002 plane showed no change for coal coked in an oven at 750°C over the raw high volatile coal. The peak was over twice as high for coke formed at 950°C showing that graphite formation was favored at elevated temperatures. The graphite peak was almost entirely missing in the samples that were run through the plasma flame. The subbituminous coal had no graphite peak before or after it was reacted.

Over 95 percent of the volatile matter as determined by the A.S.T.M. method was driven off at 750°C, but still the graphitic nature of the coal was unchanged. This supported the theory that the volatile matter in coal is attached to a matrix which has some graphite character. The rigorous conditions of the plasma jet did more than break off groups from the basic coal structure. Even though as much as 20 percent of the volatile matter remained, the whole matrix appeared to have been rearranged to leave only amorphous carbon.

Conclusions

From the flash heating and the plasma pyrolysis it appears that the volatile matter in coal reacts in a different manner than the non volatiles. Apparantly the volatile matter is not tied chemically to the coal matrix and the heat from the photo flashtube or the plasma easily volatilize this material.

In the flash heating experiments the material designated as B is highly aromatic and is a reaction product of the non volatiles in the coal. Y on the other hand is not as aromatic and is produced from the volatile material.

In the plasma experiments the acetylene conversion amounted to up to 12 percent of the coal. The yields from the subbituminous coal were considerably less. Hydrogen cyanide production was on the order of one percent for both coals. The acetylene yields doubled for both the high volatile and subbituminous coals when the plasma contained 12 percent hydrogen. The addition of hydrogen to the nitrogen-argon plasma had no effect.

The lower product yields in the plasma experiments on subbituminous coal were probably related to the higher oxygen content. Coke and activated charcoal were unreactive in the plasma jet, and so it was concluded that only the volatile matter in the coal was reacting to form acetylene and hydrogen cyanide. However, x-ray data showed that the graphitic nature of coal and coke were destroyed in the plasma jet indicating that their whole structure was destroyed.

Water-quenching the plasma reactions did not improve yields on a distilled volatile matter basis, and it reduced yields considerably on a total coal basis. All catalysts which were tried caused a reduction in product yields.

Plasma temperatures from 3000°K to 8100°K were obtained. There was, however, no relationships established between the temperature and the amount of coal converted to acetylene. This was true because the plasma temperatures were higher than the temperature for the most favorable production of acetylene. The products were probably formed after the plasma passes into the cooling chamber, and so the initial plasma temperature was not the most important factor.

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TABLE II

Run Number	3a	5a	6A	7A
Sample	hv	sub	hv	sub
Sample Feed (gr/min)	2.14	2.44	2.88	2.94
Volatile Matter Lost (%)	58.49	52.63	21.33	0.75
Gas Volume (liters)	291.5	333.8	313.2	298.8
Plasma Temp. (^{o}K)	7100	5700	4400	5800
Gas Composition (%)				
H_2	3.19	4.58	4.52	6.09
CH_4	0.20	0.26	0.15	0.14
C_2H_2	0.78	0.69	0.36	0.23
HCN	0.17	0.14	0.08	0.05
NO	--	--	--	0.09
CO	2.50	3.66	3.10	3.42
CO_2	0.05	0.14	0.54	0.84
% of Coal Converted To:				
H_2	1.76	2.21	2.26	2.56
CH_4	0.83	0.98	0.60	0.48
C_2H_2	5.27	4.25	2.33	1.24
HCN	1.19	0.88	0.55	0.28
CO	18.18	24.61	21.98	20.16
CO_2	0.57	1.43	6.00	7.74
Total	27.80	34.36	33.72	32.46

TABLE III

Run Number	3a	5a	6A	7A
% of Volatile Matter				
Lost Converted To:				
H_2	5.66	8.23	21.88	738.92
CH_4	2.83	3.66	5.80	141.12
C_2H_2	17.94	15.48	22.54	364.70
HCN	2.73	1.57	2.58	39.62
CO	28.56	42.15	101.67	2736.58
CO_2	0.53	1.45	22.54	620.90
Total	58.25	72.54	170.30	4641.84

TABLE IV

Run Number	14B	3c	5c	8C
Sample	sub	hv	sub	hv
Volatile Matter Lost (%)	24.77	91.71	71.21	33.42
Gas Volume (l)	278.0	398.1	321.8	364.5
Plasma Temp. (°K)	5700	7000	7800	7100
Gas Composition (%)				
H_2	2.08	3.56	7.03	5.31
CH_4	0.19	0.04	0.27	0.13
C_2H_2	0.15	0.38	0.86	0.42
HCN	----	0.56	0.58	0.05
NO	0.13	---	--	0.52
CO	3.37	0.71	3.37	0.25
CO_2	0.00	0.04	0.13	0.78
% of Coal				
Converted to:				
H_2	3.13	3.33	2.68	13.01
CH_4	1.02	0.31	0.82	2.52
C_2H_2	2.31	4.02	4.20	13.30
HCN	----	7.01	2.92	1.65
CO	49.84	9.34	17.77	8.74
CO_2	14.05	0.06	1.06	41.48
Total	70.85	24.67	29.45	80.70

TABLE V

Run Number	14B	3c	5c	8C
% of Volatile Matter				
Lost Converted To:				
H_2	27.75	7.32	7.50	84.71
CH_4	14.35	0.66	2.31	15.66
C_2H_2	18.66	10.13	11.78	82.52
HCN	--	7.14	4.05	4.92
CO	204.00	9.46	23.00	25.02
CO_2	33.92	0.04	0.81	72.81
Total	298.68	34.75	49.45	281.64

TABLE VI

Run Number	9C	2d	3d	6D
Sample	sub	hv	sub	sub
Volatile Matter Lost (%)	3.88	88.00	53.58	6.52
Gas Volume (l)	231.1	441.0	463.0	309.1
Plasma Temp. (^{o}K)	7900	6800	6700	8000
Gas Composition (%)				
H_2	9.28	3.75	5.00	7.95
CH_4	0.32	0.08	0.32	0.24
C_2H_2	0.31	0.37	0.54	0.14
HCN	0.08	0.75	0.52	--
NO	0.28	--	--	0.35
CO	2.16	0.81	2.56	1.58
CO_2	1.33	--	0.14	1.48
% of Coal Converted To:				
H_2	2.88	3.53	1.74	3.30
CH_4	0.80	0.60	0.89	0.81
C_2H_2	1.23	4.51	2.43	0.76
HCN	0.34	9.38	2.44	--
CO	9.54	10.60	12.34	9.24
CO_2	8.48	--	1.08	13.66
Total	23.63	34.02	20.88	27.77

TABLE VII

Run Number	9C	2d	3d	6D
% of Volatile Matter Lost Converted To:				
H_2	161.24	8.45	6.50	112.26
CH_4	44.55	1.37	3.31	27.73
C_2H_2	68.95	10.32	9.06	25.75
HCN	9.18	10.32	4.38	--
CO	246.70	11.20	21.24	145.07
CO_2	129.59	--	1.10	126.77
Total	660.22	41.66	45.59	437.58

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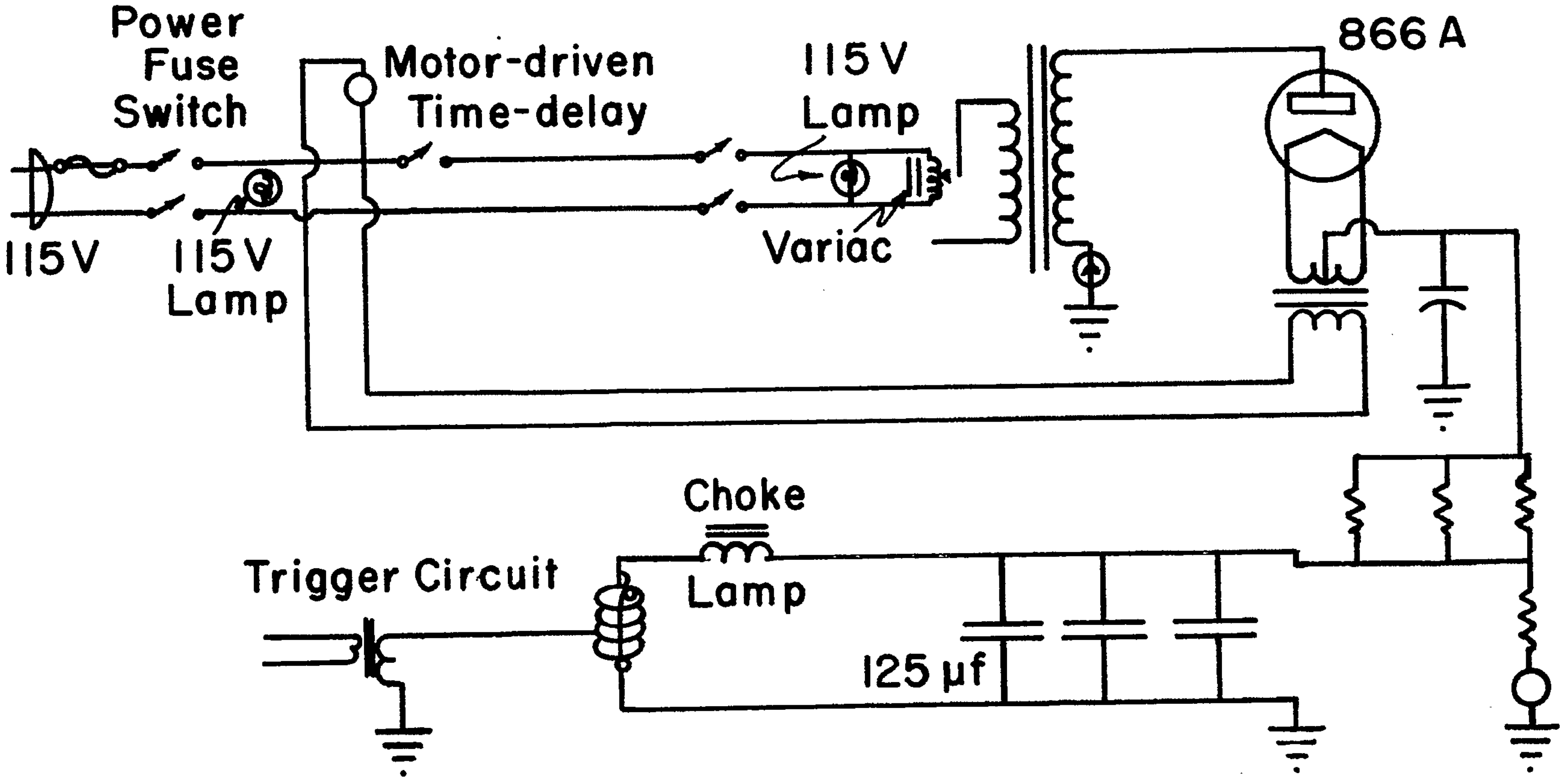

Fig. 1. Circuit diagram for photoflash unit.

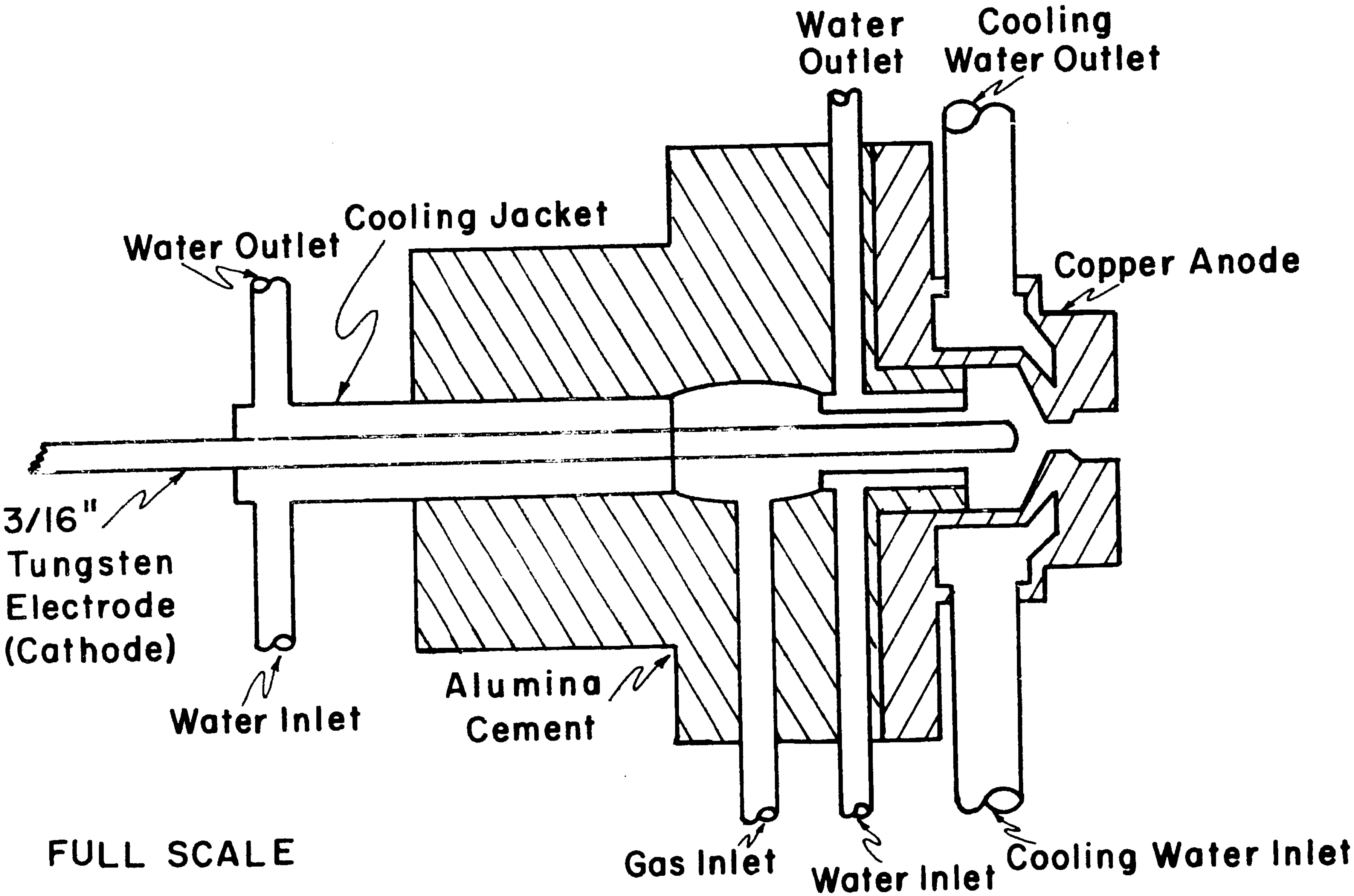

Fig. 2. Plasma jet.

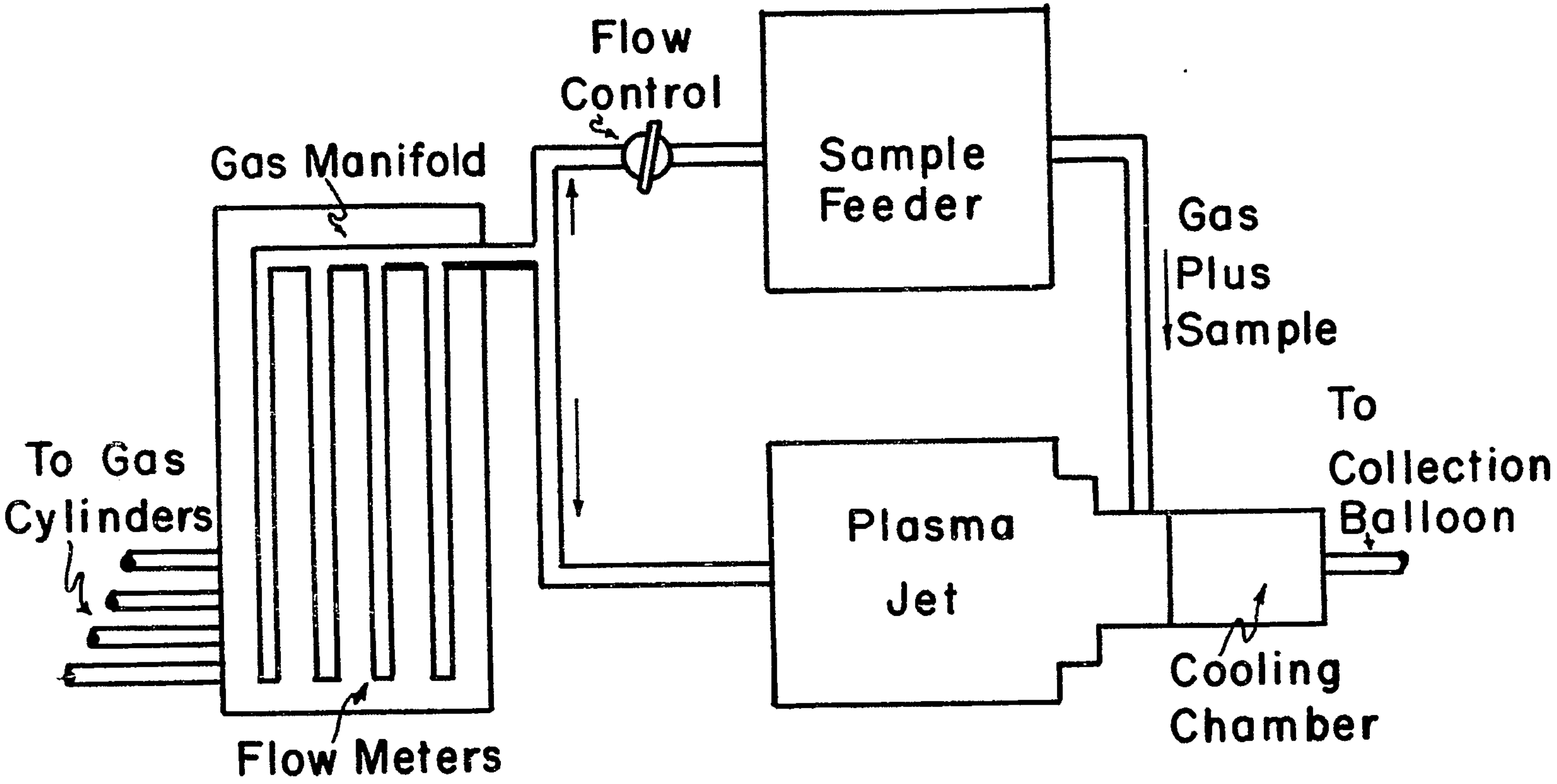

Fig. 2a. Schematic diagram of gas flow and sample feed.

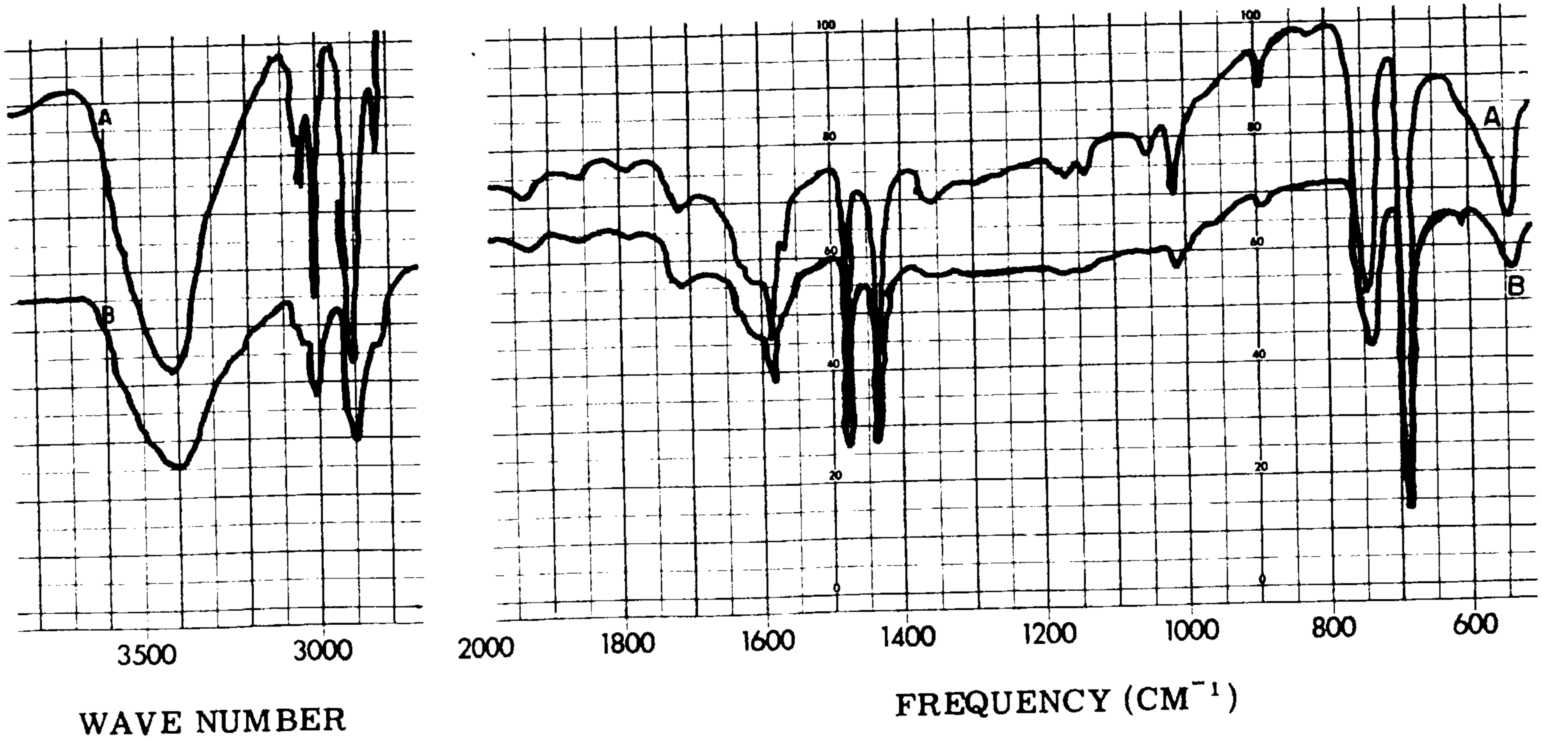

FIG. 3. IR SPECTRA OF B FLASHED AT HIGH AND LOW VOLTAGES; A-B FROM 3000-VOLT FLASH, B-B FROM 1500-VOLT FLASH.

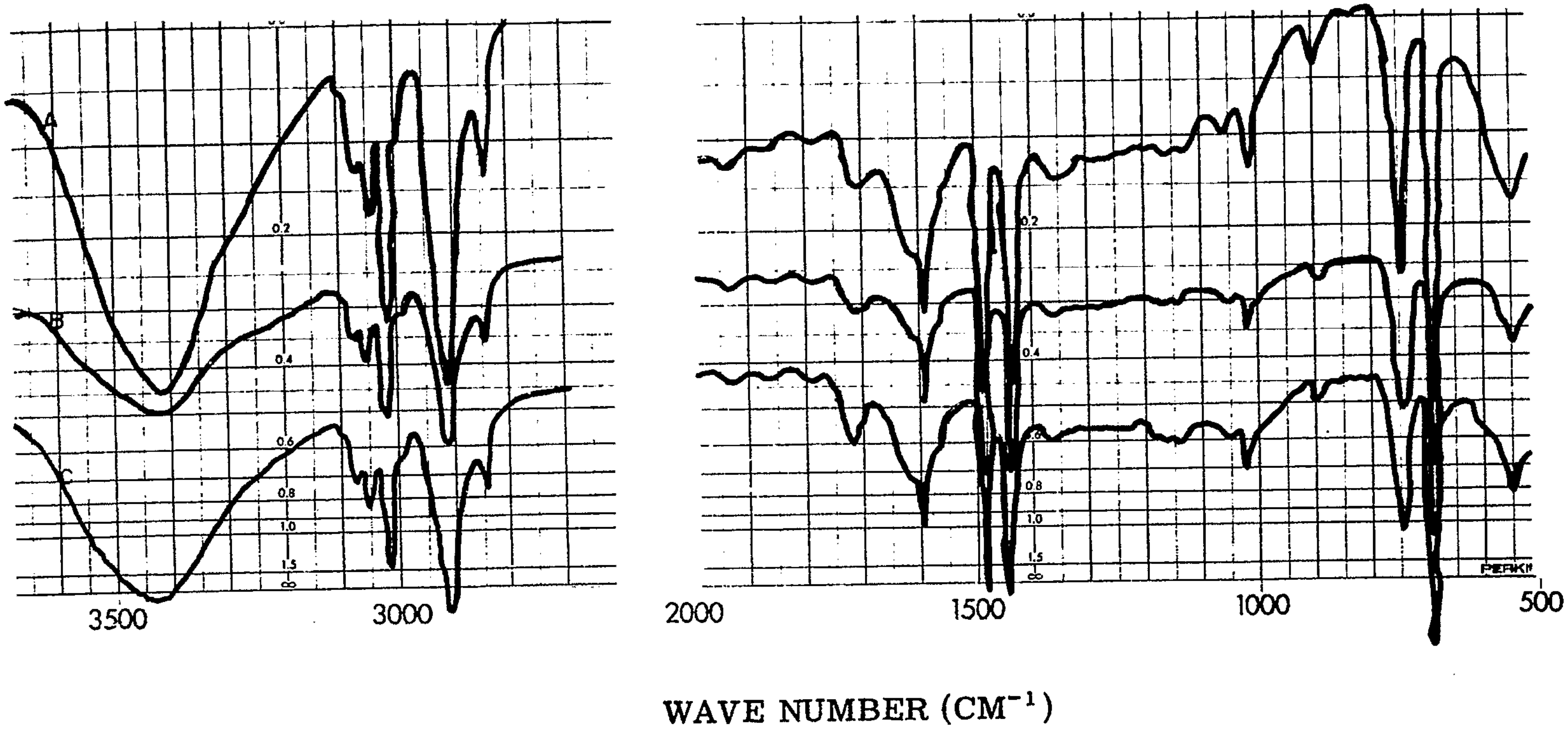

FIG. 4. IR SPECTRA OF COALS, A - SPRING CANYON COAL, B - BCR NO. 1031, C - BCR NO. 1007.

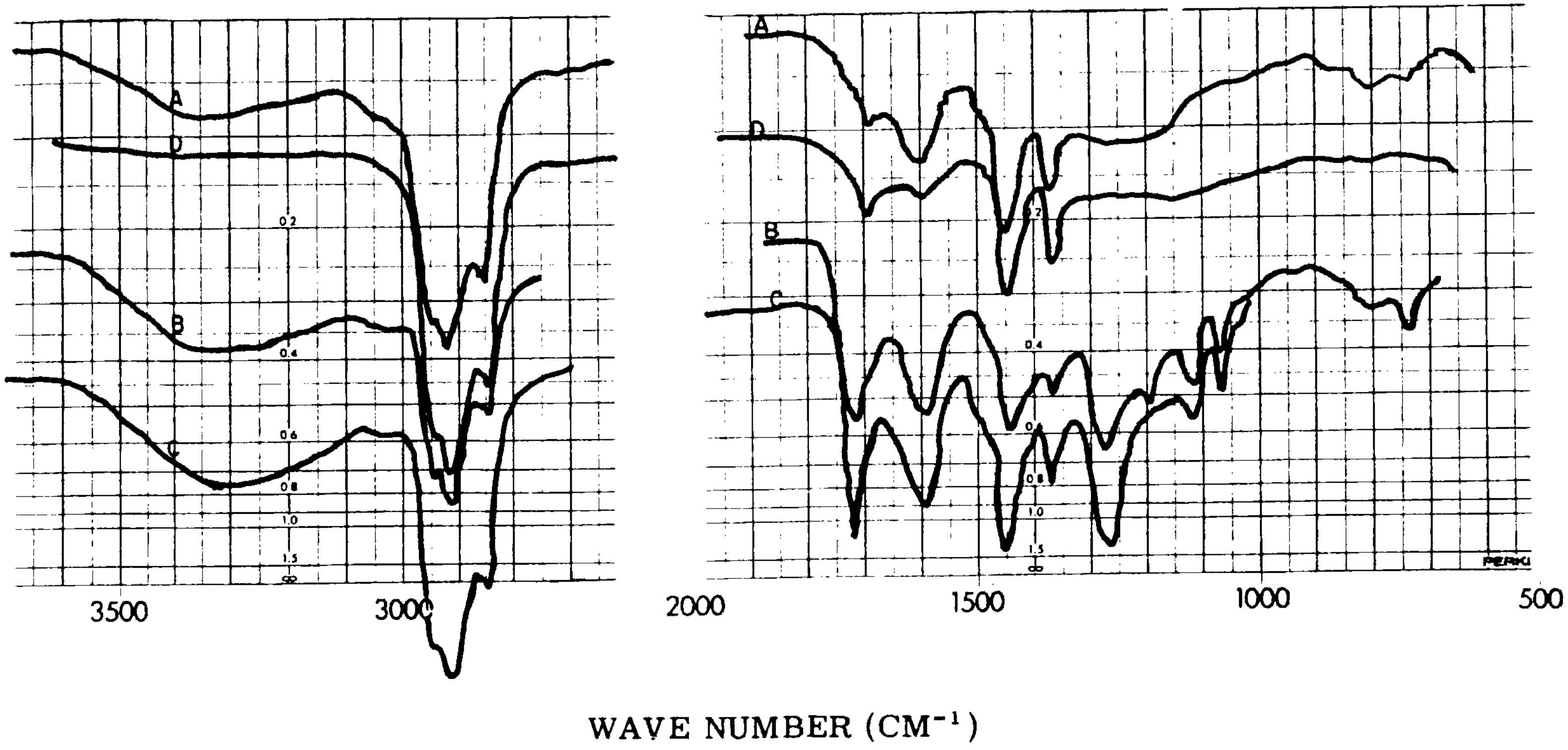

FIG. 5. Y SPECTRA FROM SPRING CANYON COAL.

A-Y DISSOLVED WITH BENZENE;
B-Y DISSOLVED WITH ACETONE;
C-Y SOLUBLE IN ACETONE AFTER BENZENE WAS USED:
D-Y SOLUBLE IN BENZENE AFTER ACETONE WAS USED.

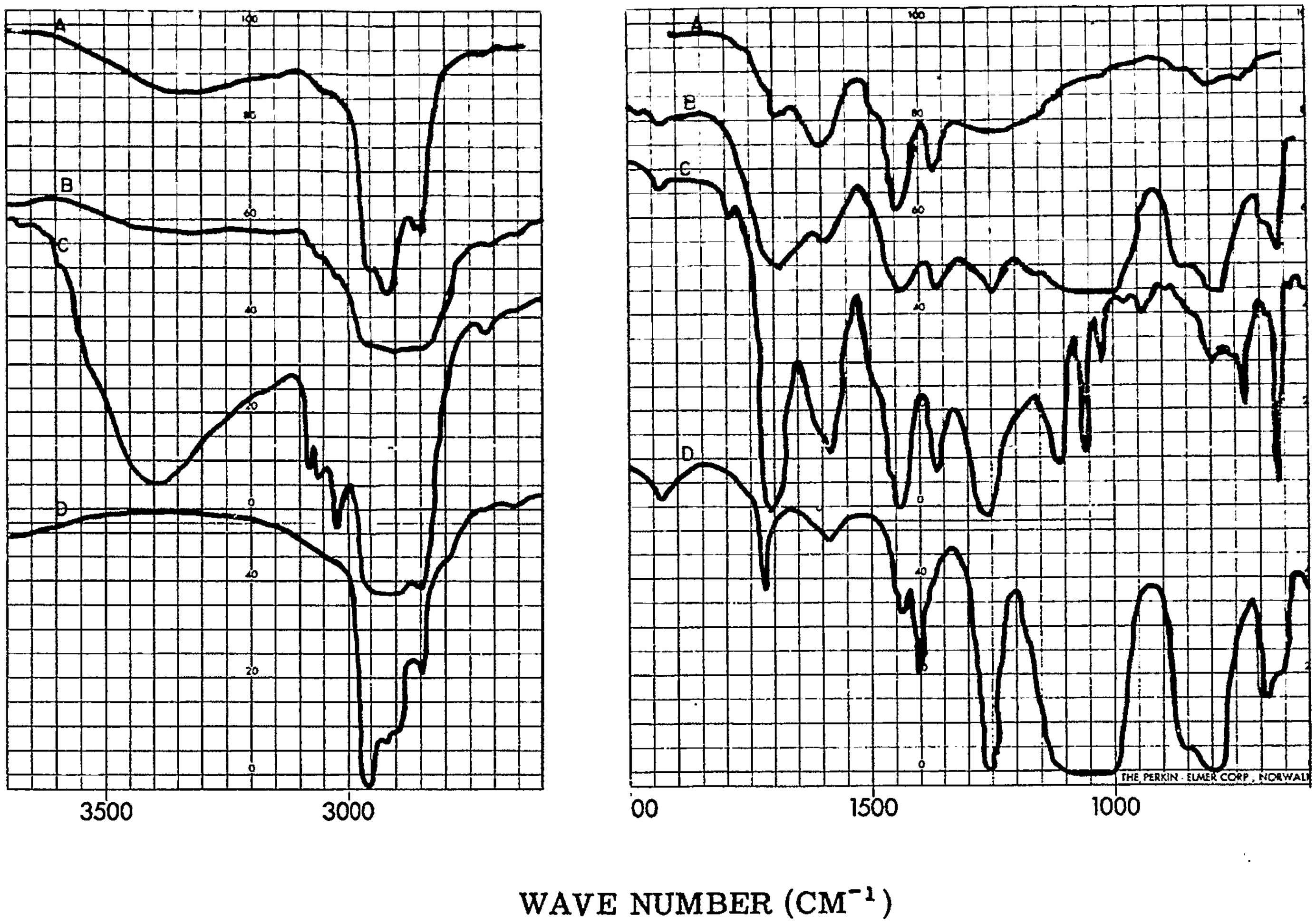

FIG. 6. IR SPECTRA. A-Y DISSOLVED IN BENZENE FIRST;

B - EXTRACT FROM COAL (COLD BENZENE;

C - BENZENE SOLUBLES FROM LOW-T COAL TAR;

D - A CLEAR OIL SEPARATED FROM Y WHEN IT WAS HEATED TO 100°C.

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A KINETIC STUDY OF COAL EXTRACTION BY TETRALIN WITH ULTRASONIC IRRADIATION

by

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Larry L. Anderson
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and
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TECHNICAL REPORT
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ABSTRACT

This investigation was concerned with the kinetics of coal extraction by 1,2,3,4-tetrahydronaphthalene (tetralin) under the influence of ultrasonic waves.

The coal used in this study was obtained from the working face of the Utah Spring Canyon Mine. The extraction of coal has been carried out at five different temperatures: 24°C, 29°C, 34°C, 44°C, and 54°C. At each of these temperatures the yield of extract increases rapidly in the early stages of extraction, levels off later to approach an asymptotic value. Analysis of the data from this study showed that a modified first-order rate equation best describes the kinetics of the extraction process.

In this study on the solvent extraction of coal, the enthalpy of activation (6.0 kcal/mole) was found to remain constant throughout the extraction process. However, an increase in free energy of activation $(\Delta F^{\ddagger})$ that was observed is accounted for by a decrease in entropy of activation. The values of free energy of activation were found to be 24.5 kcal/mole during the early stages of the extraction process and 25.1 kcal/mole near the end of the extraction process.

An experiment was conducted to see if tetralin undergoes decomposition when subjected to ultrasonic irradiation for 20 hours. The results show that no significant decomposition of tetralin occurs during the first 15 hours under ultrasonic irradiation and less than one percent of the tetralin was found to be decomposed at the end of 20 hours.

INTRODUCTION

Solvent extraction of coal has been extensively studied by various investigators, but many aspects of the action of organic solvents on coal are still unexplained. Through these studies, however, researchers have been able to separate one or more of the individual chemical substances from coal or at least they have been able to separate main organic constituents from coal. Also, through these studies the physical and chemical properties of coal, the constitution of coal, and the action of solvents on coal are better understood.

In the work for this thesis, a kinetic study was made of the solvent extraction process for removing organic substances from coal with the aid of ultrasonic irradiation. The extraction of coal was carried out at or near room temperature. It is well known that the low temperature extraction of coal offers the mildest and most appropriate method for studying the behavior of coal towards dissolution. Solvent extraction at low temperatures provides a means of separating organic compounds from coal without substantially changing their composition. In this investigation 1,2,3,4-tetrahydronaphthalene (tetralin) was used as a solvent to extract organic materials from coal under ultrasonic irradiation. Ultrasonic irradiation was employed to accelerate the rate of the extraction process. Littlewood (1) has studied the extraction of coals with pyridine using ultrasonic irradiation. He found that by placing the extraction vessel at a nodal point in a high-intensity ultrasonic beam the rate of extraction of the vitrain component of bituminous coals with pyridine was greatly accelerated. He also found that the amount of extract was dependent upon: (a) the distance of the extraction vessel from the quartz disk which produced the ultrasonic vibrations; (b) the thickness of the extraction-vessel diaphragm; (c) the input power to the generator; and (d) the rank of the coal. He concluded that at the intensities employed in his work the effects of ultrasonic irradiation were essentially of a physical nature; that is, the ultrasonic irradiation degraded materials to smaller sizes so that they were more readily dispersed. Littlewood, also, concluded that the effects of ultrasonic degradation are twofold: the first effect was the temporary breaking of the loose gel network of the van der Waals bonds between adjacent molecules; and the second effect was the actual breaking of the chemical bonds to give smaller molecules than those originally present.

From a subsequent study on solvent extraction with ultrasonic irradiation of Alberta coals, Berkowitz (2) estimated that between 15 and 40 percent of the sonic energy available at the extraction vessel can be used. Kirby, and Sarjant (3) support this view by similar conclusions from their solvent-extraction studies on a series of bituminous coals.

The ultrasonic generator employed in the research for this thesis operates with an input power of 125 watts. An X-cut quartz-crystal transducer, driven by the generator, gives vibrations of 40 Kilocycle/sec. which are transmitted from a copper membrane to the water bath holding the extraction vessel.

For this study on solvent extraction of coal, only one kind of coal, a sample from the Utah Spring Canyon Mine, was used. The particle size of the coal used was -270 +330 mesh. The following experimental procedures were followed throughout the study: (a) the coal sample was kept at the same moisture content by drying at 105°C under vacuum in an oven for three hours before performing an experiment, (b) the extraction vessel (a 25-ml. Pyrex flask) was always placed at the same position in the ultrasonic field during extraction, and (c) the coal to solvent ratio was kept constant. In this way the effect of other variables which might affect the extraction process are minimized so that the extraction of coal depends primarily on the temperature and the extraction time.

In the experimental part of this study data were obtained on the variation of the rate of extraction with the extraction time. The fraction of coal extracted up to a given time was evaluated by subtracting the weight of coal residue which is left in the thimble after extraction, followed by fractionation with benzene and trichloroethylene with a Soxhlet apparatus, from the weight of the original coal.

Not many views concerning the kinetics of the low-temperature extraction of coal with the aid of ultrasonic energy can be found in the literature. Therefore, in this work some effort was expended to obtain a better understanding of the mechanism and kinetics of the solvent extraction process. As a consequence of this work, a new model for the mechanism of coal extraction is proposed.

LITERATURE REVIEW

While there is a great amount of published literature on coal extraction in the absence of an ultrasonic field, very few articles can be found on coal extraction which describes the effect of ultrasonic energy on extraction. Since it is generally believed (1) that the basic process of extraction is the same in the presence or absence of ultrasonic energy, the conventional extraction process will be discussed first in this literature survey. Later the specific effect of ultrasonic energy on extraction will be examined.

One of the first extensive studies on solvent extraction of coal was published by Massily (5) in 1860. He used boiling chloroform, ether, alcohol and carbon disulphide as solvents. A review of the early literature up to and including the year 1950 is available in the classical monograph by Dryden (6). The application of ultrasonic energy to solvent extraction of coal was introduced by Littlewood (1). A more current review of this subject is found in the book, "The Chemistry of Coal Utilization" edited by Lowry (7).

Effect of Experimental Variables on Yield of Extract for Conventional Extraction Proccesses

Extraction time In the initial stage of the extraction process; the extraction of organic material from bituminous coal proceeds at a very high rate. The curve showing the relation between the yield of extract and time deflects after a period of a few hours and becomes substantially a straight line, which makes a very small angle with the horizontal axis (8). Deppeler and Borchers (9) studied the extraction of finely ground, high-volatile coal with tetralin under pressure and found that a parabolic curve fitted their results for up to seven hours extraction time. It is generally observed that the initial extraction is very rapid in comparison with the rate after a few hours (6). This is most noticeable during the extraction of lower rank coals with pyridine.

Temperature It has been shown (10) that the yield of extract obtained from a particular coal with a specific solvent depends only on the temperature at which the extraction is conducted and does not appear to be affected by the method of extraction employed as long as it is mechanically efficient. The effect of temperature is most marked for benzene type solvents. Dryden (11) concluded that ethylenediamine extracts half as much material from low-rank bituminous coals at room temperature as it extracts at its boiling point (116°C).

Kiebler (12) has stated that data for solvent extraction of coal with three types of solvents (benzene, pyridine, aniline) can be correlated by the following equation:

$$x = \alpha + \beta P_i$$

where x is the yield of extract, P_i is the internal pressure of solvent, and the parameters α and β are functions of temperature. The parameter β increases approximately linearly with temperature, and α does likewise up to a temperature of 220 to 250°C, but the rate of increase with temperature above this value becomes much more rapid.

Particle size of coal The dependence of the yield of extract on the particle size for the effective extraction solvents differs from that for the less effective extraction solvents (8). Yields tend to increase when the particle size of coal to be treated is reduced (13, 6). The greatest yields of extract are obtained on coals that are milled to a particle size of about one micron.

Moisture and atmospheric oxygen The presence of moisture in the solvent and oxygen in the extraction apparatus both tend to decrease the yield (13). The efficiency of extraction of coals by alcoholic potash and by ethylenediamine is reduced by the presence of water (14). However, the presence of moisture does not appear to be critically important with the majority of solvents that are immiscible with water.

Pretreatment of the coal Illingworth (15) in 1922 observed that preheating of a low rank coal to 210°C increased the subsequent rate of extraction with pyridine at its boiling point, but did not affect the ultimate yield. Walther and Steinbrecher (16) obtained maximum yields of extract with pyridine after preheating the coal to 250°C. Oxidation of coal matter by pretreatment with air at atmospheric or slightly higher temperatures, up to about 100°C, also, influences the yield from the extraction process. The results from some studies reported are somewhat contradictory on this subject.

Nature of the solvent

Physical properties of the solvent The solubility of a solid in a liquid with which it forms an ideal solution, one which obeys Raoults law, can be predicted in terms of the melting point and the heat of fusion of the solid (17). Losikow (18) and Dryden (11) pointed out that one of the functions of solvents is to swell the coal. Agde and Hubertus (19) attempted to determine if the amount of solvent absorbed by coal was related to the function μ^2/ε, where μ is the dipole moment and ε the dielectric constant of the solvent. Their results were too few to enable them to arrive at a conclusion about this, but solvents with μ of about 2.5×10^{-18} e.s.u. and ε of 13 to 20 were found to be most effective. Among those tested was acetone. Pertierra (20) agrees that the relation between yield and internal pressure of the solvent at a given temperature is approximately linear.

Chemical structure of solvent Pew and Withrow (21) have suggested that the solvent power is related to the presence of hydroxyl groups. Dryden (6) showed that primary aliphatic amines, with or without aromatic substituent, share with pyridine and certain other heterocyclic bases an abnormally high solvent power. Crussard (22) and Dryden (11) treated solvent extraction by benzene or pyridine as proceeding by two mechanisms. Orchin and Storch (23), extracting coal at about 400°C, found that a solvent with a two-ring system containing a hydroxyl group attached to an aromatic ring was a very effective solvent. Substitution of a radical for the hydrogen in bond-linkage groups, such as OH, NH, NH_2 increased the solvent power (with aliphatic amines at lower temperatures, the reverse is true). There is evidence that for coals containing less than 90 percent carbon the unshared electron pair in the solvent interacts, thus releasing heat, with some oxygen-containing group in the coal which is exposed to solvent action (24).

Rank of coal

Solvents of the benzene type Peters and Cremer (25), Muller, Graf, and Gruber (26), and Dyakova and Davtyan (27) extracted coal with trichloroethylene, tetralin, and naphthalene, respectively. All of these authors report an increase in yield of extract with decreasing rank of coal. Fisher, Peters, and Cremer noted a conspicuous exception to this observed trend (28). They found that results reported by Bakes (29), an increase in yield with an increase in rank of coal, was reversed when a coal of a still higher rank, a Welsh dry steam coal, was extracted.

Dyakova and Davtyan (27) found that for coals with a carbon content greater than about 88 to 89 percent, or less than 25 percent volatile material, the amount of extract obtainable decreased rapidly with an increase in carbon content. For coals with a carbon content lower than this limit, no definite trend in amount of extract yield with rank has been observed.

<u>Solvents of the pyridine type</u> Using pyridine as an extractive solvent, Baker found an increase in yield with decrease in rank of the coal (30). The samples used by Baker ranged from anthracite to Durham coal. Dryden (6), using ethylenediamine, found it to give a more rapid increase in rate of extraction of 85 to 87 percent carbon coal than other solvents. Bone and Sarjant (31) found that pyridine-type solvents gave the opposite effect with two coals in the medium volatile range. A coking coal yielding more extract than a lignite was found by Malanowicz (32). Cockram and Wheller (33) found in the case of American Pittsburg seam coals an overall decrease in yield with an increasing carbon content of up to 86.5%, followed by a more rapid decrease in yield for coals with higher carbon content.

<u>Extraction products</u> There is general agreement that the swelling and agglutinating properties of coal are attributed to materials found in the extract, particularly in the γ-chloroform soluble fraction

of pyridine extract, and that the residue by itself is almost or entirely inert in this respect. Bakes (29) states that the β -fraction of some coals undoubtedly cokes (residue of γ-fraction) on heating and he concludes that this fraction may be important in promoting swelling. In compounds consisting largely of hydrocarbons of large molecular weight, traces of basic and acidic bodies were found. Kuznetzov (34), who determined cryoscopically the average molecular weight of a pyridine extract (β and γ) in an unspecified solvent, obtained values of between 560 and 617, depending on the concentration, for the molecular weights of compounds in the extract. Asbury (35) found that the extract solution obtained with aniline at 225°C and phenol at 250 to 300°C contains numerous particles smaller than micron size in Brownian motion. Tetralin extracts prepared at 250 to 400°C contained only relatively large motionless aggregates. Biggs (36) concludes from data on extraction of coal by benzene under pressure that the fundamental coal unit has a molecular weight of the order of 300, and that the larger units are held together by relatively weak linkages. Dryden (11) reports that ethylenediamine extract prepared at atmospheric pressure contains particles a few hundred Ångstroms in diameter.

The Effect of Ultrasonic Irradiation on Extraction of Coal

According to Weissler (37), a sound wave of high intensity (10 watts/sq.cm. at a frequency of 1 Megacycle/sec.) travelling through water imparts to the molecules an amplitude as small as 10^{-5} cm. However, the water molecules are accelerated to values about 250,000 times that for acceleration due to gravity. The maximum instantaneous velocity is about 40 cm./sec., and the pressure at a given point in the water varies over a range of about 5 atmospheres. Obstacles in the path of the wave experience a repulsive force along the direction of propagation because of the "radiation pressure" of about 1 g./sq.cm.

One effect of the great changes in pressure (between ± 5 atm.) is the development of cavitation. Cavitation leads to the formation and violent collapse of small bubbles or cavities in the liquid as a result of pressure changes (1). According to Freundlich and Gillings (38), there appears to be an optimum ultrasonic intensity that coincides with maximum formation of cavitation voids. For intensities above this value, further increases in power will cause a decrease in yield. This can be best explained on the basis of the scattering of energy by the numerous bubbles in the extraction vessel, and the removal of dissolved gases so that the residual amount is insufficient to maintain extraction at its maximum rate. The other explanation is that this enormously intense ultrasonic wave possibly causes the destruction of the solvent structure, separation of the extracted materials from the solvent, etc.

Littlewood (1) concludes that the effects of ultrasonic degradation are twofold. The first effect is believed to be the temporary breaking of the loose-gel network of van der Waals bonds between adjacent molecules, and this does not take place to any appreciable extent in the absence of cavitation. The inter-molecular van der Waals forces are of the order of 1 to 10 Kcal./mole. The second effect is the actual breaking of chemical bonds to give smaller molecules than those originally present. These chemical bonds have bond strengths in the range of 50 to

100 Kcal./mole. In support of these views, Lockwood et. al., (39) and Stacey (40) state that the trend in ultrasonic degradation is towards a preferential cleavage of components of higher molecular weights before fragmentation of lower molecular weight components commences.

This review of the literature revealed that Berkowitz (41) was the first to report the use of an ultrasonic field to a coal-solvent system. He noted from the results of a subsequent study of Alberta coals that the utilization efficiency of the sonic energy varies between 15 and 40 percent at a frequency of 0.25 Kc./sec. Consequently, he stated that the major portion of the energy was merely reflected from the surfaces of the coal particles and that unless the greater portion of the absorbed energy was regarded as being concentrated at specific bonds, such as weak van der Waals inter-molecular bonds, it was quite inadequate to break such bonds. Kirkby, Lakey, and Sarjant (42) used a low-intensity ultrasonic generator at a frequency of 880 Kc./sec. in their extractions of a series of bituminous coals (mesh size: -300 +330) using pyridine. They concluded that under identical conditions: (a) the percentage extraction of a variety of coals (9.1%, 12.6%, 19% for 802, 701, 401 N.B.C. coals, respectively) bears a close relationship to their chemical compositions; (b) the extraction of coals with polar solvents can be accelerated by the application of a ultrasonic field of low-intensity (0.1 watts/sq.cm.) insufficient to induce cavitation in the carrier liquid or to bring about chemical degradation; (c) the total amount of extract is dependent upon the temperature of extraction; (d) the rate of extraction is highest with smallest particle size; and (e) the penetration of the ultrasonic vibrations appears to be limited to the external surface of the coal particles.

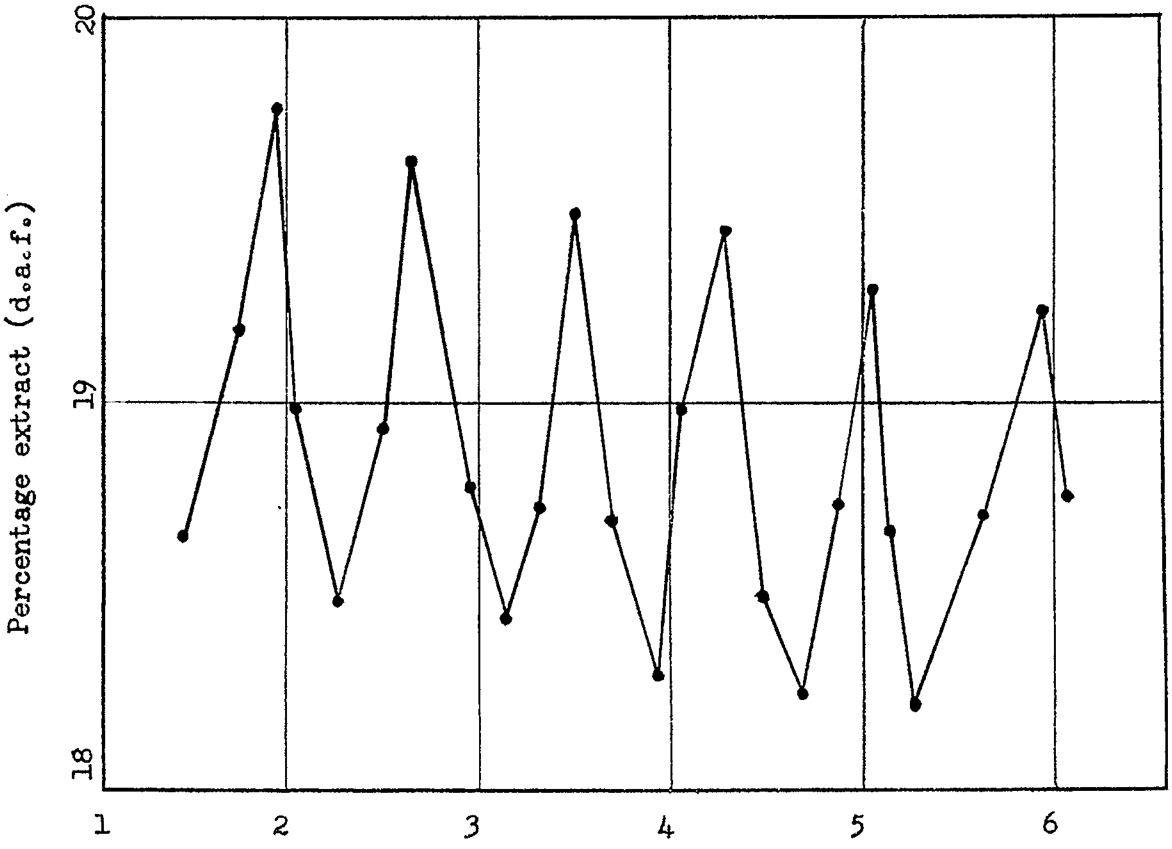
Brown and Rybicka (43) used ultrasonic irradiation in the extraction of coals with solvent mixtures, such as equi-molecular proportions of acetophenone/monomethylformamide and monomethylcyclohexanone/dimethylformamide. They found that the maximum yields of extract compared favorably with those obtained with ethylenediamine. With an ultrasonic output equivalent to 50 watts they were able to extract 44 percent of the extractable material from a coal in 15 minutes at room temperature compared with 31 percent in 60 hours at 100°C using a Soxhlet apparatus.

Van Vucht, et. al., (44) in an attempt to prepare dispersions of coal particles which have sizes smaller than 1/20 of the wave length of the irradiation used in a mulling agent suitable for examination by infrared spectroscopy, subjected a suspension of coal in n-heptane to the cavitating action of an ultrasonic field generated by magnetostriction of a nickel tube. They found that at a frequency of 10 Kc./sec. 300 mg. of coal could be reduced to a particle size of less than half a micron in one hour. With anthracites, however, cavitation caused no disintegration whatsoever.

According to the literature stated by Loomis and Richards (45), the maximum amount of sonic energy is transmitted to a solid-liquid system if the extraction vessel is placed at a nodal point in the sonic beam, and if the diaphragm of the extraction vessel vibrates with a frequency equal to that of the quartz disk producing the oscillations.

It was found by Littlewood (1) using a 72 mesh size coal to position the extraction vessel accurately in the transformer oil above the quartz disk in order to obtain a maximum yield of extract. The graph of Fig. 1 (based on Littlewood's work), shows how the distance of separation between the extraction vessel and transducer affects the yield of extract from coal. It can be seen from the graph of Fig. 1, (a) that the maximum yield of extract coincides with the positions of the nodal points, (b) that these maxima decrease with increasing distance from the quartz disc, and (c) that the sound energy which passes through a barrier is a maximum when the thickness of the extraction vessel in the transducer corresponds to an integral number of half-wavelengths. The effect of input power on the yield of extract is shown for several British coals (classified with N.B.C. Code no.) by the curves of Fig. 2. The data used for preparing the graph of Fig. 2 are those reported by Littlewood (1). As the input power to the quartz transducer was increased over the range of about 15 to 225 watts, the yield of extract for a four-hour irradiation period increased to a maximum somewhere in this range and then decreased as power was increased to higher levels.

The main features of the curves shown in Fig. 2 are as follows: (a) For coals with carbon content in the range of about 84 to 89 percent, the input power required to obtain a maximum yield of extract remains constant at about 200 watts, but for lower-rank coals (containing 82 to 83 percent carbon) maximum yield is obtained at lower input power. For a higher-rank coal with 92 percent carbon the maximum yield is obtained for an input power of 40 watts and for coals with carbon contents above 92 percent the maximum yield of extract is obtained at a much lower value of input power. (b) Extrapolation of the curves to the ordinate of zero watts illustrates the effect of rank on the degree of extraction. Coals of lower rank usually give higher yields. (c) In the case of the code 206 coal containing 92 percent carbon, the yield of extract decreases as



Distance of extraction vessel from transducer, mm.

Fig. 1. Effect of attenuation in transformer oil on yield of extract.

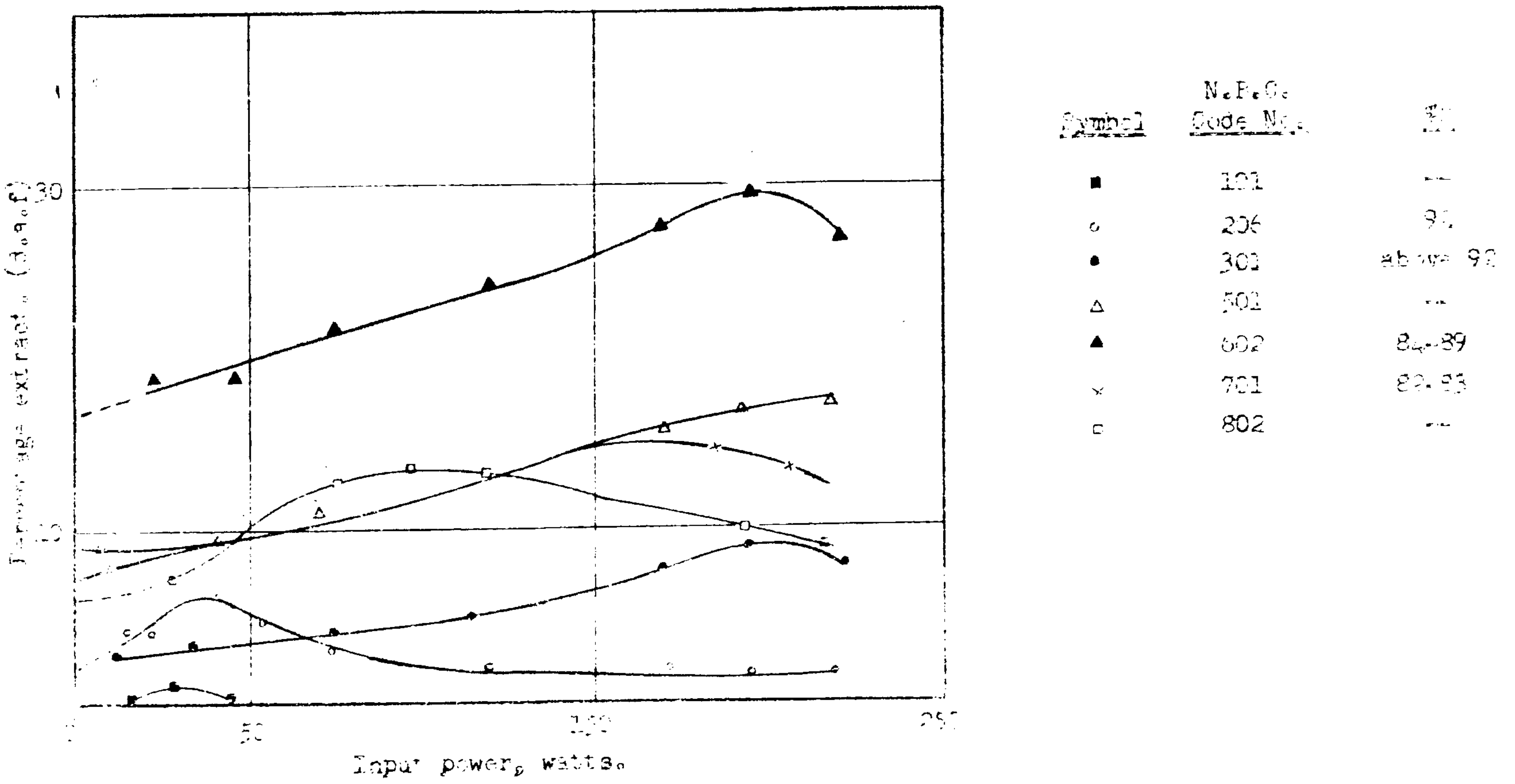


Fig. 2. Effect of input power on yield of extract.

Symbol	N.P.G. Code No.	[illegible]
■	101	--
○	206	92
●	301	above 92
△	501	--
▲	602	84-89
×	701	89-93
□	802	--

input power is increased to a constant value which more or less coincides with the value obtained by extrapolation of the curve to the ordinate of zero watts. The results shown in Fig. 2 are best explained by assuming that three important processes, solution, dispersion and agglomeration, are occurring simultaneously. Agglomeration and subsequent separation do in fact take place during extraction in an ultrasonic field, but the effect is often marked by the dispersive action of cavitation.

The results of Fig. 3 indicate that ultrasonic irradiation during the extraction process does not produce any chemical effects. The two spectra are shown in Fig. 3 on extracts from coal. One extract was obtained using ultrasonic irradiation and the other was obtained by simply allowing the coal to stand in contact with pyridine for the requisite length of time. The spectra were recorded by Littlewood (1) with a Grubb Parsons model S3A double beam spectrometer in which the samples were examined as 0.2 percent extract in potassium bromide disks. Since the reference beam was in each instance set to give 100 percent transmission without the sample, the spectra are directly comparable. This again lends weight to the conclusion that the effects of a high-intensity ultrasonic field on extraction are essentially of a physical nature. It is concluded that at the intensities used, physical degradation is the sole effect of ultrasonic irradiation, leading to sizes of material that are readily dispersed in pyridine. This analysis is probably also true for the observations reported by Berkowitz (41) and Ayre (46). Their explanation is based on thixotropic properties, and is possibly in error because many thixotropic systems exhibit the opposite property of rheopexy (47); i.e. the solidification time is decreased (and not increased as they suggested) if the sol is

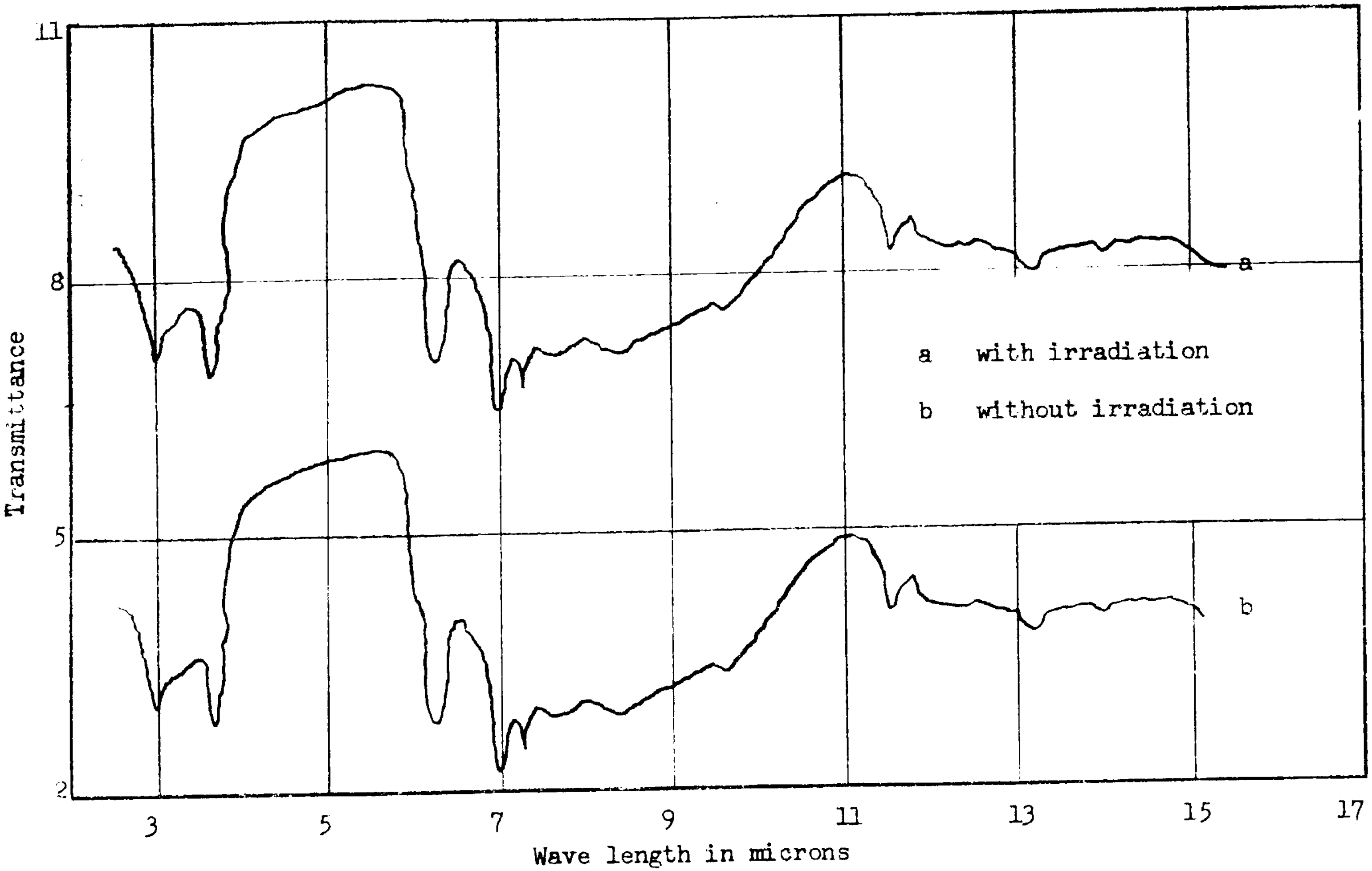


Fig. 3. Infra-red spectra of the extract of Aldwarke 501 coal.

subjected to a more or less uniform mechanical vibration. Berkowitz (41) stated that an ultrasonic field was used to increase the efficiency of the extraction process at room temperature.

Mertins (48) observed that a temperature rise of 80°C for extraction of coal with pyridine in the presence of an ultrasonic field, gave a threefold increase in yield over that for a conventional extraction process when ultrasonic intensity of about 0.1 watt/sq.cm. was applied to the system. However, he stated that an upper limit of yield was eventually reached which was quite independent of any further increase in temperature. Mertins also noted that the extracts obtained at 100°C did not precipitate any of extracted material on cooling which indicates that his solutions were unsaturated. This suggests that for a given coal there is a maximum solubility of the extract in pyridine and that this maximum solubility cannot be exceeded by altering the conditions of the extraction process.

Mertins also found that: (a) the extraction of different coals by pyridine was affected to varying degrees by an ultrasonic field of the same intensity, and (b) the acceleration of the extraction process by the same increase in intensity of the field varied with different coals. Neither atmospheric oxidation of the coal, nor concentration of the solution significantly affected the amount of extract obtained for a given set of experimental conditions. He found that the presence of impurities such as benzene or water in the pyridine greatly reduced the amount of extract obtained. A very weak field of 0.1 watt/sq.cm. gave an initial rapid rate of extraction which fell off with time until no more extract could be obtained at that temperature. Extraction at higher temperatures with a weak field resulted in an increase in the maximum amount of extract. Mertins concluded that the ultrasonic field does not disperse material which is otherwise insoluble. The effect of particle size of coal on the amount of extract was also investigated and it was found that the effect of the field on the rate of extraction increases with a decrease in particle size.

Mechanism and Models Proposed for Coal Extraction

The kinetic mechanism of the solvent extraction of coal proposed by Oele (8) has been widely used in correlating kinetic data. He assumed that the reaction proceeds with a zero-order forward reaction which was immediately followed by a first-order backward reaction. He believed the backward reaction to be the precipitation of the dissolved coal particles back to the crystal form.

The differential equation that describes the mechanism is:

$$\frac{dx}{dt} = k_f - k_b x \tag{1}$$

integration of Eq. (1) yields:

$$\ln\left(1 - \frac{k_b x}{k_f}\right) = -k_b t \tag{2}$$

at equilibrium

$$k_f = k_b x_{eq} \tag{3}$$

and by substitution

$$\ln\left(1 - \frac{x}{x_{eq}}\right) = -k_b t \tag{4}$$

where k_f is the rate constant for the forward reaction, k_b is the rate constant for the backward reaction, and x is the fraction of coal extracted.

By plotting $(1 - \frac{x}{x_{eq}})$ versus time on a semi-log graph paper, k_b for each temperature can be found; and from $x = \frac{k_f}{k_b}$ at equilibrium, k_f for the corresponding temperature can be calculated.

Another mechanism of solvent extraction of coal has been suggested by Hill, Hariri, Reed, and Anderson (49). They describe their model as follows. A coal particle is considered to be permeated by the solvent through its macro and micro pores, and the other materials lodged in the coal are then accessible to the action of the solvent, tetralin. There is experimental evidence (50, 51) supporting this mechanism. The ultra-fine structure of the pores has vacancies of the order of a few Ångstroms in diameter. Also, larger capillaries and fissures are present. Because different kinds of microstructure are found in a coal particle, several different kinetic mechanisms for coal extraction are possible.

According to the mechanism suggested by Hill et.al. (49) the dissolving out of the organic material from the coal is the diffusion of the solution of organic materials in tetralin out of the pores into the main body of the solvent surrounding the coal particle. This is considered as first order process with respect to both the coal and the solvent. The hydrogen transfer reaction will be considered as a second order process since the transfer reaction from the tetralin to the coal will not be a prominent process at the temperature of the experiment. A kinetic expression describing a concurrent reaction of the first and second order must be used. The kinetic expression describing this process is:

$$\frac{dx}{dt} = k' (a_i - x) + k_2 (a_i - x)(b_T - x) \qquad (5)$$

where a_i is the initial concentration of the coal and b_T is that of tetralin, k' is the first-order reaction rate constant, and k_2 is the second-order reaction rate constant. The other symbols have their usual definition. Integration and simplification of Eq. (5) gives

$$2.303 \log \left(\frac{a_i}{a_i - x}\right) = \frac{x}{b_T} + t(k' - k_2 a_i + k_2 b_T) \qquad (6)$$

From an Arrhenius plot of their data, $k' = 10^{12.8}\ e^{-50.0/RT}$, sec^{-1}, and k_2 for the extraction of the interspersed materials in the coal is $9 \times 10^5\ e^{-26/RT}$, sec^{-1}

Hill and Lyon (52) have proposed the following model for coal. The high-volatile coal consists of large alkylated, polynuclear, oxygenated, aromatic and heterocyclic nuclei. The porous structure of the coal matrix is held together by three-dimensional tetrahedral bonds with some oxygen and sulfur.

It is believed that the first material that is transferred from the coal into solution is that trapped in coal pores which may be weakly bonded to the main coal structure. It requires the least amount of activation energy to dissolve the coal present in this form. The remaining micelles of coal are strongly bonded. A higher activation energy is required to break these bonds. As the extraction process continues, the activation energy for extraction of coal increases. Accordingly, Hariri (4) proposed the following reaction mechanism for the thermal dissolution of coal based on his study.

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1. coal $\xrightarrow{k_o} R_o + L_o + G_o$

2. $R_o \xrightarrow{k_1} R_1 + L_1 + G_1$

3. $R_1 \xrightarrow{k_2} R_2 + L_2 + G_2$

n. $R_{n-2} \xrightarrow{k_{n-1}} R_{n-1} + L_{n-1} + G_{n-1}$

where k_o is greater than k_1, k_1 is greater than k_2 ....., and k_{n-1} is greater than k_n.

In the first, unimolecular reaction R_o is the solid coal, L_o is the liquid, and G_o is the gas. When this reaction is well advanced the first reaction becomes the main route for the extraction of R_1 (with the rate constant k_1), and so on. His experimental data did not fit the simple, first-order reaction.

$$\frac{dx}{dt} = k'(1 - x)$$

because the rate constant k' was found to be a linear function of x. Th rate equation that described his data was:

$$\frac{dx}{dt} = k_o' \,(1 - sx)(1 - x) \qquad (7)$$

where s is a constant that is equal to the reciprocal of the maximum possible fraction of extract (x_m) obtainable. When Eq. (7) is integrate with the initial condition t = 0, x = 0, one obtains:

$$\ln \frac{1 - x}{1 - sx} = (s - 1)k_o't \qquad (8)$$

EXPERIMENTAL PROCEDURES AND RESULTS

The experimental results obtained from extraction studies on coal are somewhat dependent on the experimental procedures employed. Several different experimental methods have been used by different investigators for extraction of coal. The experimental procedure described in this section was found to be best for this study.

Coal preparation The coal sample selected for this study was taken from a working face of the Utah Spring Canyon Mine. The chemical analysis on this coal made by the Commercial Testing and Engineering Company is listed in the following tabulation:

Ultimate analysis

Element	Wt.%
Carbon	72.88
Hydrogen	5.58
Nitrogen	1.51
Oxygen	10.82
Sulfur	0.65
Chlorine	0.19

Proximate analysis

Component	Wt.%
Water	.....
Ash	8.37
Volatile Matter	45.71
Fixed Carbon	45.92

Heating value-----13,237 BTU/lb, calculated on dry basis.

The sample of coal was ground and sized to -270 +330 mesh. This ground coal was then kept in a stock sample bottle and stored in a desiccator.

Ash determinations on the sample of ground coal were made, and an average value of 5.97 percent* was observed which was used to correct for the available coal in the coal sample.

Sample preparation About one gram of ground coal was removed from the stock bottle and put into a beaker. The sample was then dried in a vacuum oven at 105°C for a period of three hours, removed from the oven, and then placed in a desiccator for one hour.

The sample of coal was then placed in 25 ml. Pyrex-glass flask and the weight of the coal determined by weighing on an analytical balance. (Samples of coal for all extraction runs were prepared in the same way).

Solvent preparation The solvent used for coal extraction was Practical-Grade 1,2,3,4-tetrahydronaphthalene (tetralin), manufactured by Matheson Coleman and Bell Corporation. No purifying or preparative procedure was applied to the solvent.

Extraction apparatus An ultrasonic generator, Sonogen Model AP-25-B, generating a radio frequency of 40 Kc./sec. with an average input power of 125 watts was used to drive the quartz transducer. Fig. 4 is a photograph of the experimental apparatus showing the Sonogen ultrasonic generator. The transducer converts the output of the generator into mechanical vibrations which are referred to as ultrasonic waves. The frequency of these vibrations is above the audible range. The transducer was attached to the bottom of a tank, which contains water, and into which the mechanical (ultrasonic) energy is transmitted. The average power of mechanical vibrations per unit area is 0.59 watt/cm^2.

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*This value is lower than the one given in the original analysis and is probably due to the use of a different apparatus and period of time for heating the coal.

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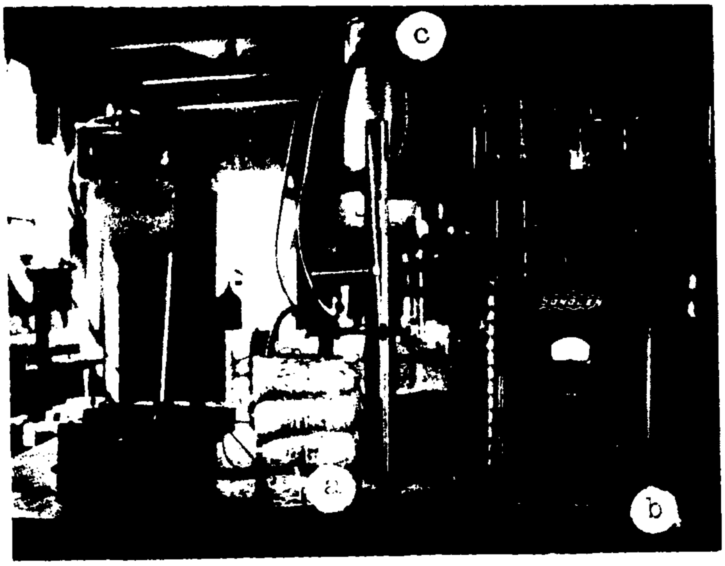

(a) Transducer.
(b) Sonogen Ultrasonic Generator.
(c) Cooling Water Reservoir.

Fig. 4. Photograph of experimental apparatus used for coal extraction studies.

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A copper stand with a height of 4.45 centimeters was specially designed to hold the extraction flask in the bottom of the tank at the nodal point of the sonic wave. A constant-head cooling water reservoir was constructed to provide cooling water for maintaining a constant temperature in the water bath during the extraction perid. The water flow was regulated by a small clamp on the hose leading from the reservoir to the cooling coil of the water bath.

<u>Determination of optimum coal to solvent ratio</u> In order to determine the best ratio of coal to solvent to be used in extraction studies, experiments were performed with different ratios of coal (in grams) to solvent (in cubic centimeters) under the influence of an ultrasonic field. For these preliminary tests the extraction time was five hours and the bath temperature was 20°C. The experimental procedure outlined below was employed in the preliminary work. The experimental results are tabulated in Table 1. As a result of the preliminary study, a ratio of solvent to coal of 50 to 1 was chosen as the ratio to be used throughout this extraction study. A plot of fraction of coal extracted, x, versus coal to solvent ratio (grams of coal/milliters of solvent) is shown in Fig. 5.

The fraction coal extracted, x, is the weight of coal extracted, ΔW, divided by the initial weight of coal, W_c, on an ash free basis.

<u>Experimental procedure</u> To a flask containing about 10 cubic centimeters of tetralin, 0.2 gm of coal was added and the covered flask was placed on the copper support in the water bath of the transducer. (The term "transducer" is used to describe the complete system composed of the water bath and quartz-crystal transducer.) The regulated cooling

water kept the transducer water at a constant temperature throughout the extraction process. (The ultrasonic generator was turned on at least forty minutes before samples were put into the transducer.) After the desired extraction time, the vessel was removed from the water bath. The contents of the flask were transferred to a weighed thimble and washed in a Soxhlet apparatus using benzene followed by trichloroethylene as washing agents. The extract from the coal was freed from the residue by extracting all the material (solution of extract and residue) for about 25 hours with benzene and about 50 hours with trichloroethylene. Extraction was normally continued until the liquid descending to the boiler was colorless. The thimble was taken out of apparatus and dried in an oven at 105 to 110°C for 24 hours.

Table 1. Extraction of coal
for different coal/solvent (C/S) ratio.
(Temperature: 20°C, Extraction Time: 5 hours)

Run No.	C/S ratio (grams/ml)	Fraction of coal extracted, x.
1	0.1	0.0715
2	0.05	0.0878
3	0.033	0.0911
4	0.025	0.0923
5	0.02	0.0909
6	0.0167	0.0915

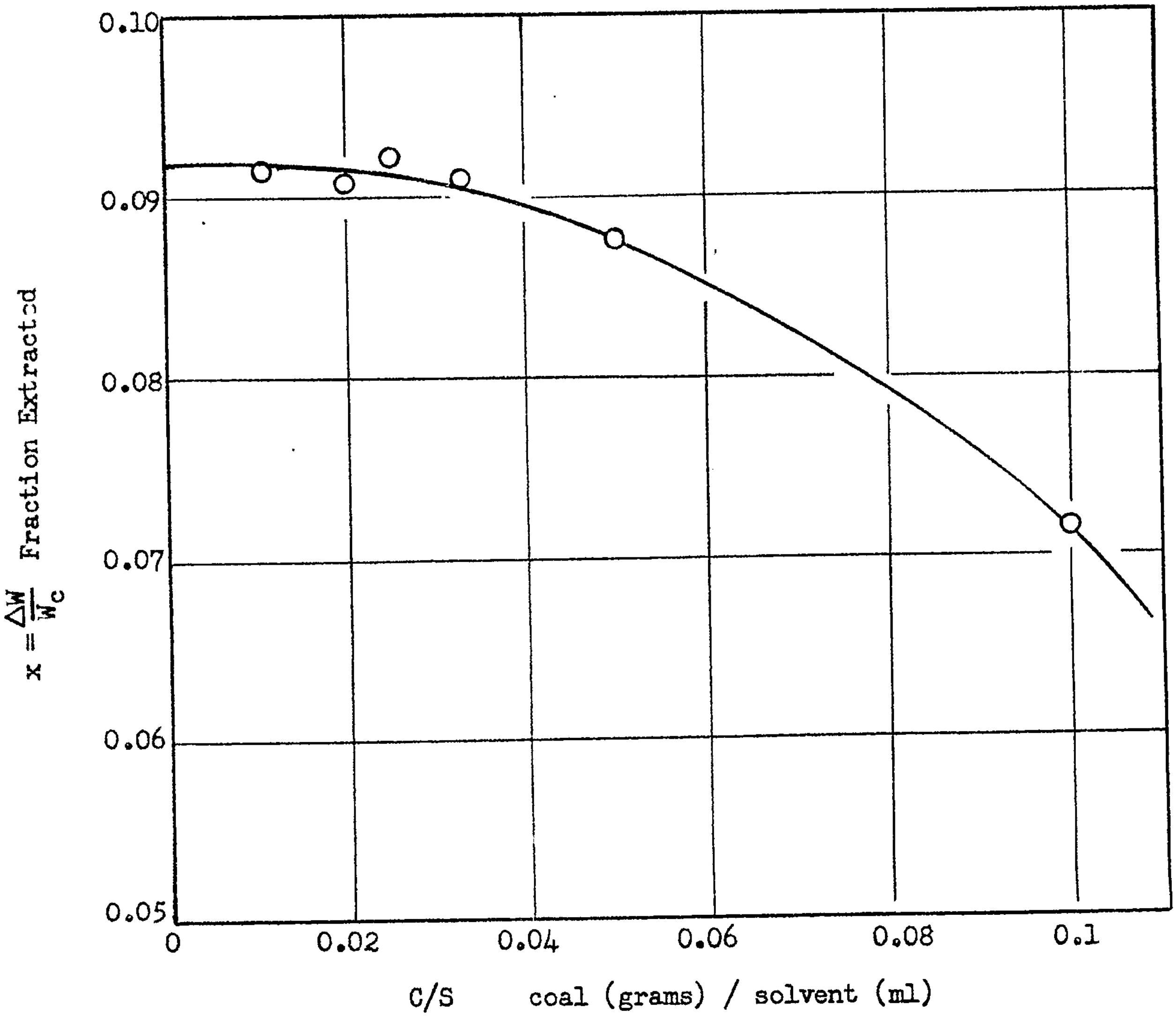

Fig. 5. Percent of extraction versus coal/solvent ratio at 20°C and 5 hours.

The dried thimble was placed in a weighing bottle and held in a desiccator for 15 minutes for cooling. The weighing bottle containing the coal residue and dry thimble was then weighed. The weight of coal residue was obtained by subtracting the weight of the empty thimble from the total weight of the coal residue, and thimble. The amount of extract was found by subtracting the weight of the coal residue from the weight of the original coal. With these data, the fraction of coal extracted could then be determined. By varying the extraction time for different samples of coal, the rate of dissolution of extractable material in the coal was calculated for use in determining the kinetics of the extraction process. For analyzing data, the fraction extracted, x, determined from four extraction experiments at the same conditions were used.

Preliminary experiments Before starting study on the extraction process for coal, the following tests were performed. (a) Experiments were conducted to determine the amount and resulting products of decomposition of the pure solvent, tetralin, in the ultrasonic field. (b) Blank extraction tests were run on benzene, trichloroethylene, benzene and trichloroethylene, and tetralin.

Decomposition of tetralin Approximately fifty cubic centimeters of tetralin were put in a 50 ml Pyrex glass flask. The flask containing the tetralin was placed in the transducer and subjected to ultrasonic irradiation. The system was maintained at 25°C for a period of five hours and then a liquid sample was taken. Next the temperature was raised to 34°C and kept at this level for another five hours. Another liquid sample was taken after this period. The same procedure was repeated for temperatures of 44°C and 54°C. The samples were then analyzed by gas chromatography*. For temperatures below 44°C, the solvent which had been under ultrasonic irradiation for fifteen hours showed a trace of decomposition. After a period of twenty hours at temperatures in range of 25°C to 54°C, there was a small but insignificant amount of decomposition of the tetralin (less than one percent). Chromatographic analysis of the original solvent showed that the solvent contained 98 percent tetralin, 0.06 percent naphthalene and 1.94 percent other impurities, which included a small amount of decalin (decahydronaphthalene).

Blank tests on benzene To a flask containing about 10 cubic centimeters of benzene, 0.2 gram of coal was added and the covered flask was kept undisturbed for one hour at room temperature. The solution and coal residue were then transferred to a weighed thimble. The extract was separated from the residue by washing in the Soxhlet extraction apparatus, using benzene as a washing agent. After the extract was completely separated from the residue (or when the overflowing liquid appeared to be colorless), the thimble was taken out and dried in an oven at 105 to 110°C for 25 hours. The completely dry thimble was then placed in a weighed weighing bottle and placed in a desiccator to cool. The bottle with the cool residue and dry thimble was then weighed. The result showed that 1.02 percent of coal was extracted by washing with benzene in the Soxhlet extraction unit.

Blank tests on trichloroethylene For this solvent, the procedure was the same as that used for benzene. The amount of coal extracted was found to be 0.37 percent.

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*The gas chromatograph used was Model 720, Dual-Column, Programmed Temperature, Gas Chromatograph made by F & M Scientific Corp.

Blank tests on benzene and trichloroethylene For this test, the same procedure was used as that for blank tests on benzene. The extract was separated from the residue by washing in the Soxhlet extraction apparatus using benzene followed by trichloroethylene as the washing agents. The result showed that 1.18 percent of coal was extracted.

Blank tests on tetralin Using the same procedure as that for blank tests on benzene, 10 ml of tetralin were used as solvent. The flasks containing the tetralin and coal were allowed to sit for one hour, five hours, and twenty hours, and then the contents of the flasks were washed with benzene followed with trichloroethylene in a Soxhlet apparatus for twenty and fifty hours respectively. The extractions were found to be 3.08, 3.26, and 3.46 percent of the coal after one, five, and twenty hours, respectively. These values are very close to the results reported by Hariri (4).

Precipitation tests on extract Experiments were performed to detect whether precipitation of the extract from the solvent, tetralin, occurs when the extraction process is continued for a longer time.

The coal sample was dried in a vacuum oven at 100°C for three hours. Four 0.2 gm samples were placed in 25 ml extraction flasks and tetralin was added to give a fixed solvent to coal ratio of 50 to 1. Flasks of mixed samples were placed in the transducer at the bath temperature of 54°C and irradiated for five hours. One of the flasks was removed after five hours. The coal residue was freed from the solution in a Soxhlet apparatus and then dried in the oven until no trace of solvent was found. The dried coal residue in the thimble was put into a weighing bottle and weighed on an electric balance. The fraction extracted was found to be 11.24 percent of the original coal. When the first flask was removed, the temperature of the water bath was lowered to 44°C. The experiment was continued for another five hours and the yield for another sample was determined. The yield was also determined for samples held at a temperature of 34°C for 15 hours of reaction time and for samples held at 24°C for 20 hours. The results are summarized in Table 2.

These data show that precipitation of the extract does not occur for longer extraction times in tetralin.

Table 2. Summary of data obtained from precipitation tests on extracts with tetralin.

Sample No.	W_i (gm)	W_f (gm)	$\Delta W \times 10^3$ (gm)	W_c (gm)	x (%)	Time (min.)	Temp. (°C)
1	0.2840	0.2540	30.02	0.2672	11.24	300	54
2	0.3207	0.2869	33.82	0.3018	11.21	600	44
3	0.3371	0.3016	35.46	0.3168	11.32	900	34
4	0.2542	0.2271	27.08	0.2394	11.31	1200	24

Coal extraction by tetralin without ultrasonic irradiation The experimental procedure described on page 26 was used for making conventional extractions on coal. The coal-tetralin mixture was only stirred during the extraction period. These experiments containing 0.2 gm. of coal and 10 ml. of tetralin were carried out at three temperatures;

24, 34 and 54°C, and samples were analyzed after five extraction periods, 2, 5, 10, 15, and 20 hours. The experimental data obtained at the three temperatures are tabulated in Tables 8, 9, and 10. The results from this study are compared with results obtained on extraction of coal in the presence of an ultrasonic field in a later section.

Coal extraction by tetralin with ultrasonic irradiation Coal was extracted by tetralin in the presence of an ultrasonic field using the experimental procedure described on page 26. Extraction experiments were performed at five different temperatures; 24, 29, 34, 44, and 54°C, and the data from these tests corresponding to these temperatures are given in Tables 11, 12, 13, 14, and 15, respectively. Extraction times were varied over the range of a few minutes to 20 hours. The data obtained from this experimental work are analyzed and the results are discussed in the next section.

DISCUSSION OF RESULTS

Analysis of Experimental Data

Oele's (8) mathematical expression for the kinetics of coal extraction (refer to page 19) is simple and convenient to use, but it fails to describe the experimental data obtained in this study. Oele's equation for kinetics of the reaction process considers a forward extraction reaction of the zero order opposed by a first-order reaction for reprecipitation of material extracted from the coal. Experimental data that fit his proposed model, when plotted in the form of $\ln(1 - x/x_{eq})$ versus time, are defined by a straight line. The data from this study, plotted in the form suggested by Oele's model, do not fit the equation obtained by Oele. Furthermore, the data obtained indicates that for the entire extraction period, the extraction solution remains unsaturated. No precipitation or recrystallization of coal was observed during the experiments of this study or in the study made by Hariri (4). It appears that the decrease in rate of extraction with time that was observed in this work can be attributed to the progressive decrease in the amount of coal that is able to dissolve in the solvent, and does not appear to be related to an increase in the backward reaction postulated by Oele (precipitation of extract from the solution).

Experimental data obtained in this study on the extraction of coal by tetralin with ultrasonic irradiation are plotted in the form of extraction time versus yield in Figure 6 for temperatures of 29 and 54°C and in Figure 7 for temperatures of 24, 34, and 44°C.

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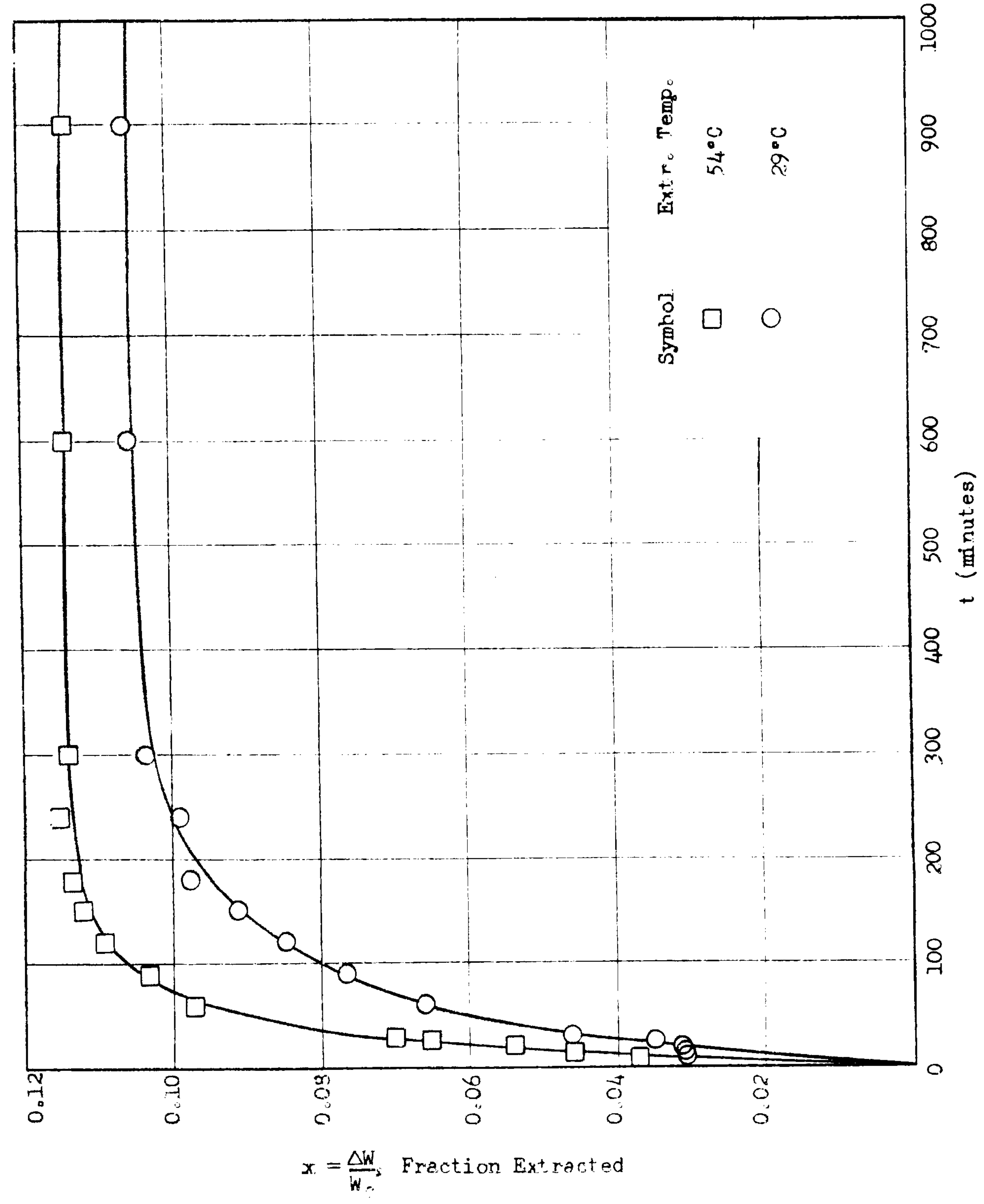

Fig. 6. Time-yield curves for extraction of coal by tetralin with ultrasonic irradiation.

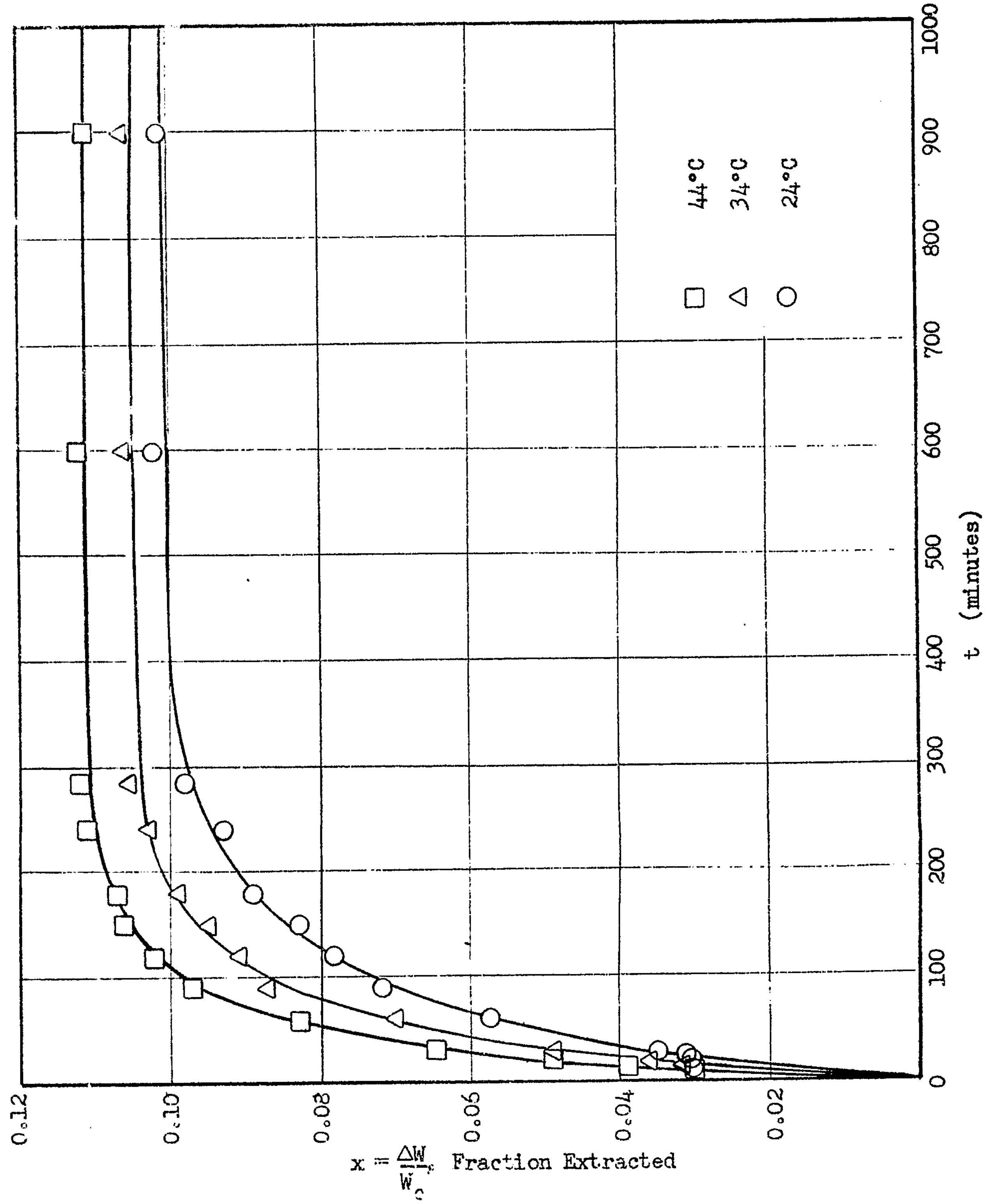

Fig. 7. Time-yield curves for extraction of coal by tetralin with ultrasonic irradiation.

Another model for coal extraction can be described as follows: In the extraction of coal by solvent, the process can be considered to proceed by two different mechanisms. One takes place at the coal-tetralin interface where the extraction reaction is the kinetically controlled step, and the other is the flow of extract and tetralin inside the pores where diffusion processes become the rate controlling step.

The model considered here has a close analogy to the oxidation of metals in which the phase-boundary reaction and diffusion reaction have been concluded in the theoretical model as two separate parallel reactions (53). Therefore, the overall process of coal extraction can be represented by the following equations:

$$\frac{1}{k_a} + \frac{1}{k_d}\frac{\Delta W}{W_c} = \frac{t}{\frac{\Delta W}{W_c}} \qquad (9)$$

Where: k_a is phase-boundary extraction rate constant,

k_d is diffusion extraction rate constant,

t is time,

ΔW is weight of coal extracted,

W_c is weight of original coal (ash free).

Fig. 8 is a plot of $\Delta W/W_c$ versus $t/\Delta W/W_c$ for extraction of coal at a temperature of 24°C. It is seen from this plot that the experimental data are not consistent with the model described by Equation (9). It appears that the parameters, k_a and k_d, may possibly be a function of $\Delta W/W_c$.

The author then employed the method of finite differences to evaluate $\Delta x/\Delta t$ for the experimental data at the five temperatures. The

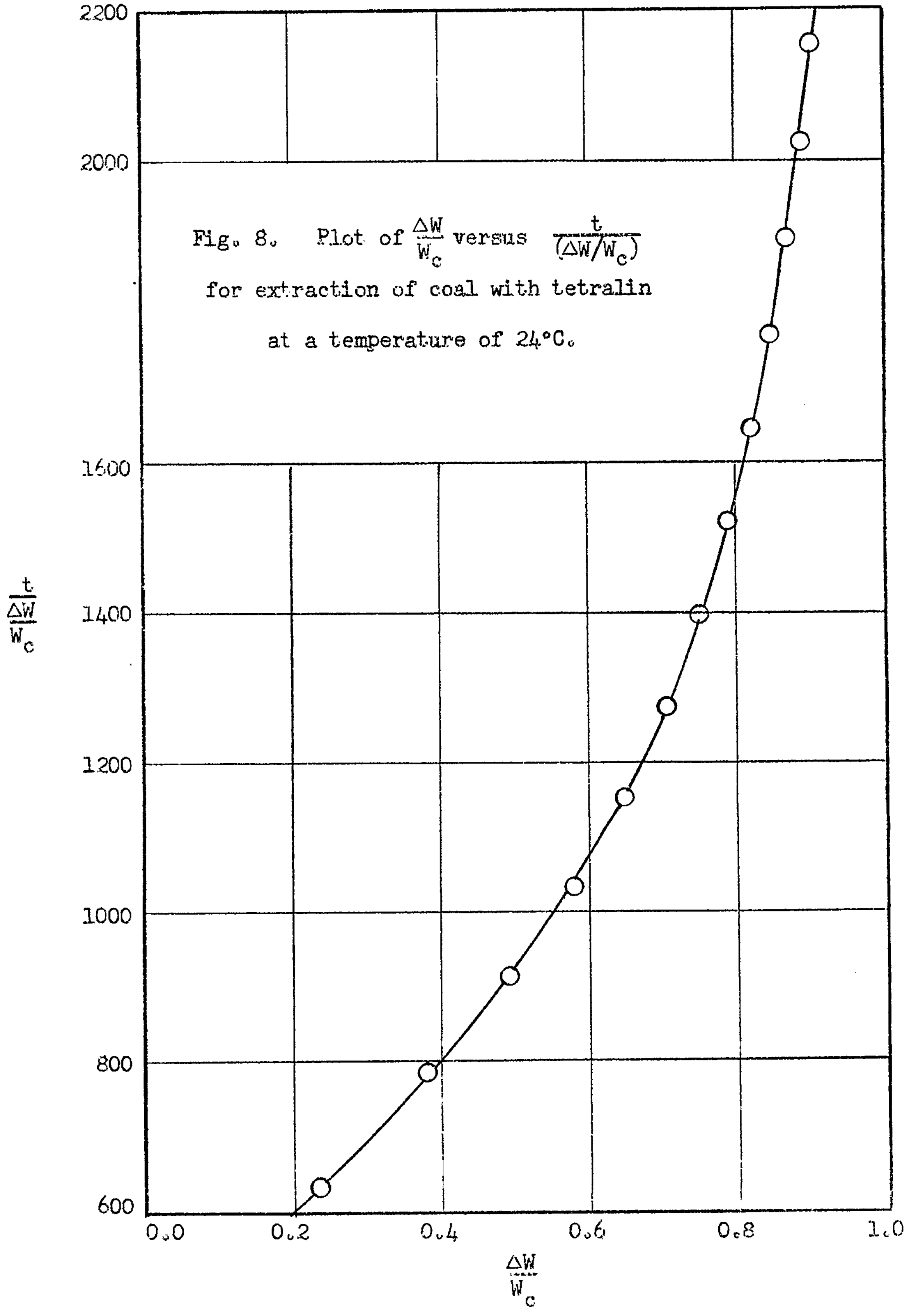

Fig. 8. Plot of $\frac{\Delta W}{W_c}$ versus $\frac{t}{(\Delta W/W_c)}$ for extraction of coal with tetralin at a temperature of 24°C.

kinetics of the extraction process were assumed to be represented by a reaction of the first order.

$$\frac{dx}{dt} = k'(1 - x) \tag{10}$$

The parameter, $\Delta x/\Delta t$, was plotted against $(1-x)$. From this graph, it was found that the data plotted as a definite curve. This implies that the parameter, k, in Equation (10) is a function, $\theta(x)$, of the fraction extracted, x. Furthermore, from Fig. 9 (the data used in preparing this graph are given in Table 3), it is found that $(\frac{\Delta x}{\Delta t})/(1-x)$ or $\theta(x)$ is a function of $x^{\frac{1}{2}}$, and the kinetic equation for this extraction process can be written in the following form:

$$\begin{aligned} \frac{dx}{dt} &= \theta(X)(1 - x) \\ &= k_o'(1- dx^{\frac{1}{2}})(1 - x) \end{aligned} \tag{11}$$

In this equation, d turns out to be the reciprocal of square root of the maximum possible yield of extract, $1/(x_m)^{\frac{1}{2}}$.

The concentration term $(1-x)$ in Equation (11) needs to be carefully considered with respect to the experimental data obtained from this study. The integer, 1, in the concentration term implies that one hundred percent of the coal is available for extraction. For the data obtained in this work, a concentration term $(a-x)$ was used for evaluating the experimental data. The value for a for extraction at a given temperature is equivalent to the maximum possible yield of extract, x_m, for a given set of conditions; and is evaluated from curves of yield versus time (see Figs. 6 and 7).

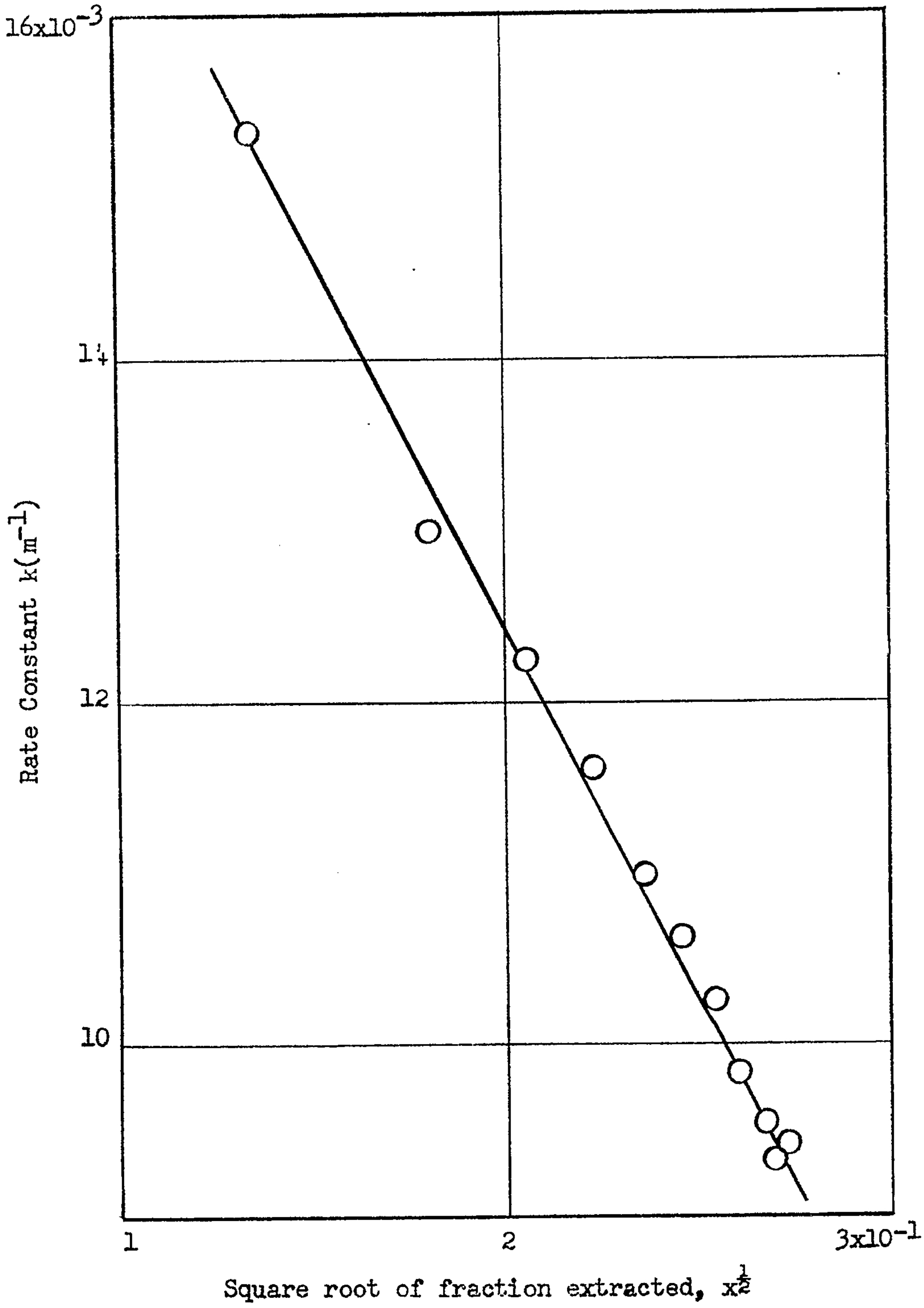

Fig. 9. A plot of $\frac{\Delta x/\Delta t}{(1-x)}$ versus square root of fraction extracted, $x^{\frac{1}{2}}$, for extraction of coal with tetralin at a temperature of 24°C.

Table 3. Variation of $(\frac{\Delta x}{\Delta t})/(1-x)$ versus square root of fraction extracted, $x^{\frac{1}{2}}$, for extraction of coal with tetralin at 24°C.

$\frac{\Delta x}{\Delta t}/(1-x)$	x	$x^{\frac{1}{2}}$
0.015	0.019	0.138
0.013	0.036	0.191
0.012	0.048	0.219
0.012	0.057	0.239
0.011	0.064	0.253
0.011	0.070	0.265
0.01	0.075	0.273
0.01	0.079	0.280
0.01	0.082	0.286
0.01	0.085	0.291
0.01	0.087	0.295

Proposed Mechanism for Extraction of Coal with Ultrasonic Irradiation

From the preliminary analysis of the experimental data, the concentration term, (a-x), was chosen as a variable concentration parameter to analyze the original experimental data.

It is first assumed that the extraction process observed is represented by a first-order reaction:

$$\frac{dx}{dt} = k'(a - x) \tag{12}$$

According to this equation, a plot of $\frac{\Delta x}{\Delta t}$ vs (a-x) should give a straight line. In the work reported in this paper, however, the plot is a curve (see Fig. 10). The first-order assumption is therefore rejected, and a second-order reaction mechanism was assumed.

$$\frac{dx}{dt} = k_2(a-x)^2 \tag{13}$$

This was also rejected because a plot of $(\frac{1}{a-x})$ versus time also turns out to be a curve instead of the straight line predicted by the integrated form of Equation (13) (see Fig. 11). The data used for Fig. 11 are listed in Table 4.

Table 4. Variation of $\frac{1}{a-x}$ with time (minutes)
for extraction of coal with tetralin at 24°C,
(a = 0.102, x = fraction of coal extracted).

t(min.)	x	a-x	$\frac{1}{a-x}$
0	0	0.102	9.8
15	0.019	0.083	12.06
30	0.036	0.066	15.24
45	0.048	0.054	18.54
60	0.057	0.045	22.25
75	0.064	0.038	26.49
90	0.070	0.032	31.25
105	0.075	0.027	36.63
120	0.079	0.023	42.74
135	0.082	0.020	49.50

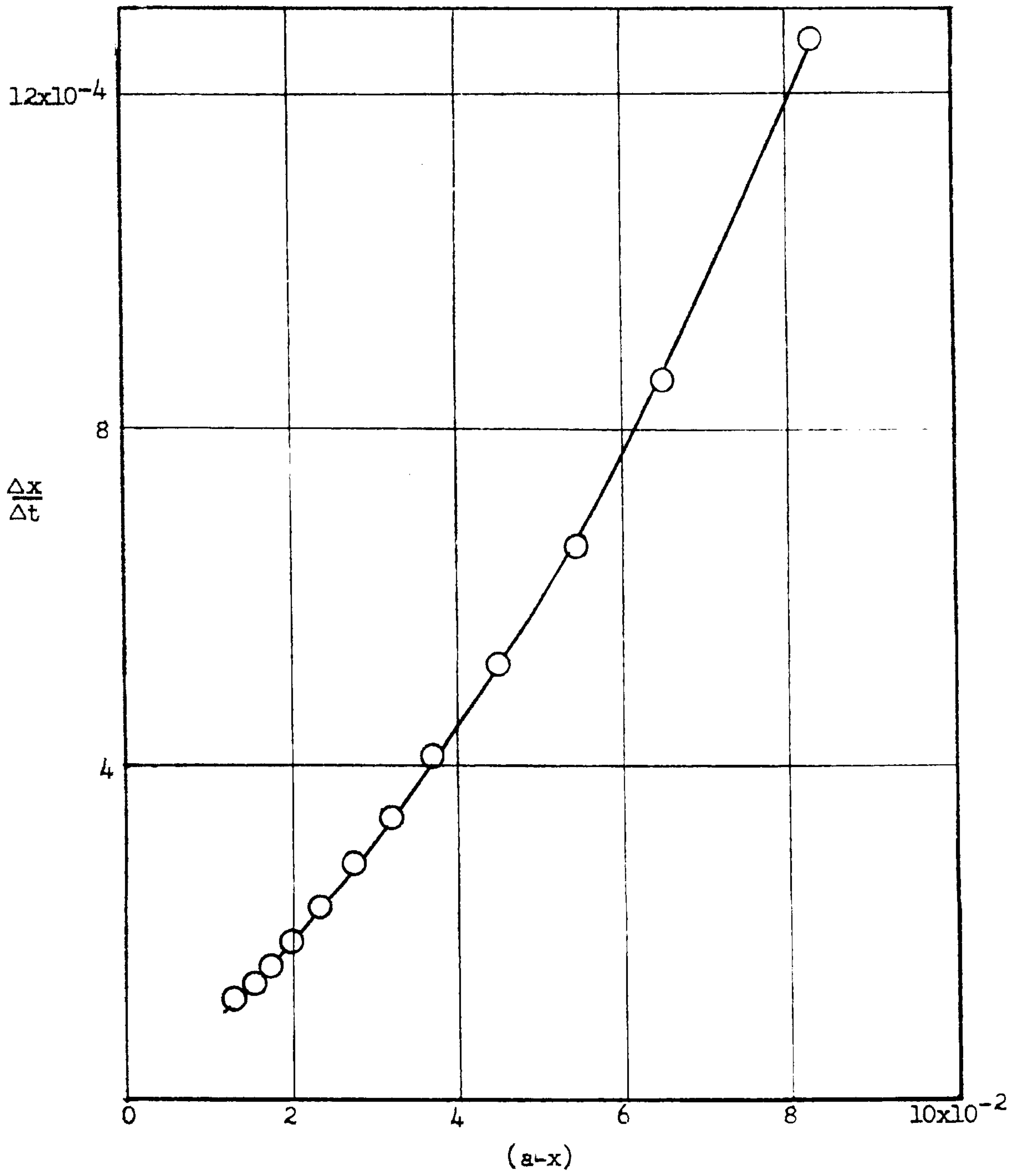

Fig. 10. A plot of rate of extraction of coal as a function of driving force to the first power. Temp. 24°C. Solvent, tetralin.

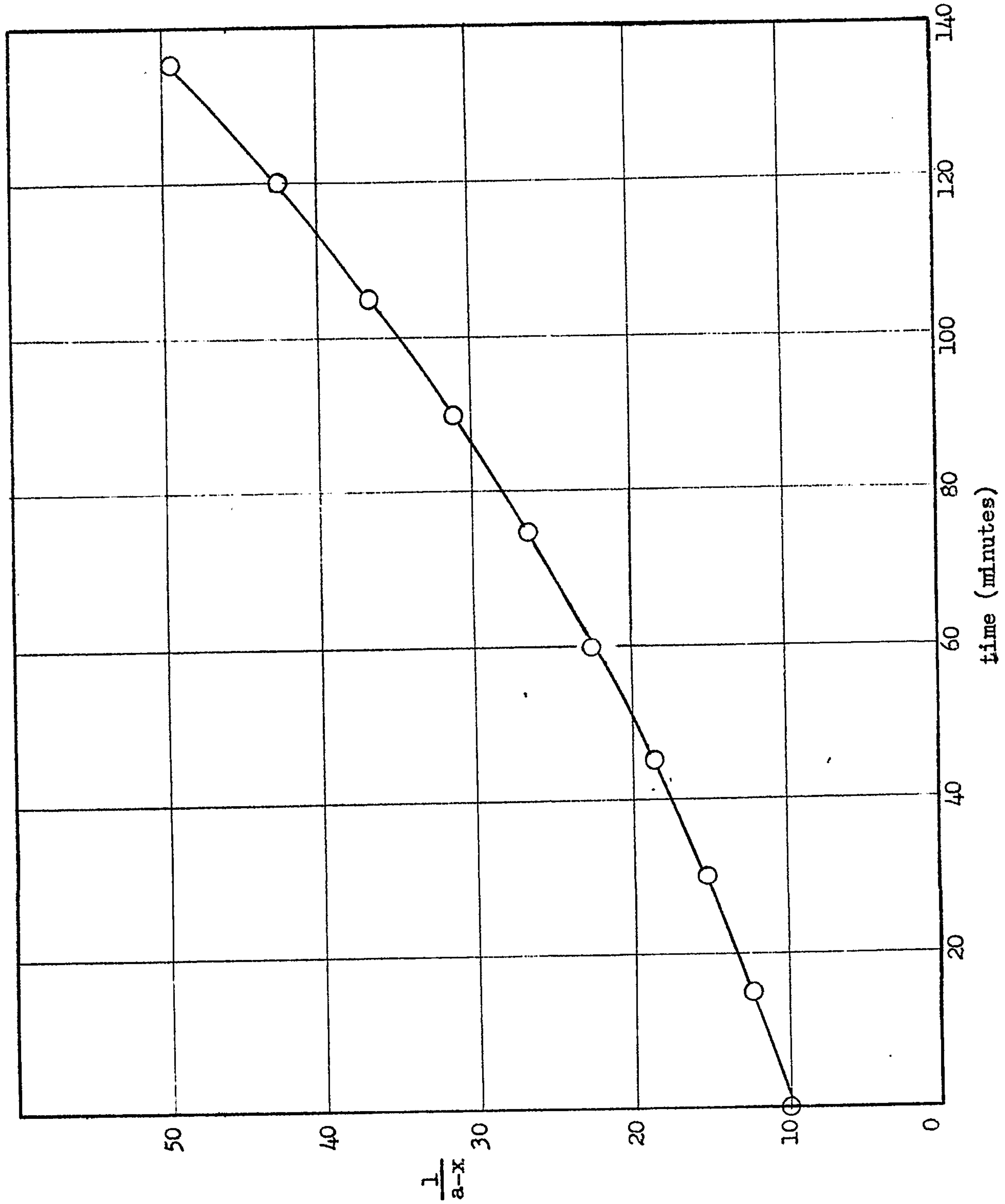

Fig. 11. A plot of $\frac{1}{a-x}$ versus t for 24°C.

When the experimental data for all five temperatures were plotted in the form of $\ln(\frac{\Delta x}{\Delta t})/(a-x)$, versus x as shown by Fig. 12, the data were well represented by straight parallel lines. Since the term $(\frac{\Delta x}{\Delta t})/(a-x)$ resembles a rate constant, the parameter, k, is used to describe it. Values for k as a function x are not hard to find from the data given in Fig. 12 (54).

$$k' = k_o e^{\frac{-b'x}{RT}} \qquad (14)$$

where k_o is the initial rate constant, and b' is a constant. The data of Fig. 12 shows this relationship is valid for about 90 percent of the extraction period.

The differential expression which describes the extraction rate for the data obtained in this study is

$$\frac{dx}{dt} = k_o(e^{\frac{-b'x}{RT}})(a-x) \qquad (15)$$

According to the Eyring's absolute reaction rate theory, the initial rate constant is given by

$$k_o = \gamma \frac{kT}{h} \exp(-\frac{\Delta F_o^{\ddagger}}{RT})$$

Hence Equation (15) can be written as:

$$\frac{dx}{dt} = \gamma \frac{kT}{h} \exp(-\frac{\Delta F_o^{\ddagger}}{RT} - \frac{b'x}{RT})(a-x) \qquad (16)$$

Where: x is weight of coal extracted/weight of original coal (ash free),

a is the maximum change in weight of original coal (ash free),

γ is transmission coefficient, assumed to be approximately 1,

k is Boltzmann constant,

h is Planck's constant,

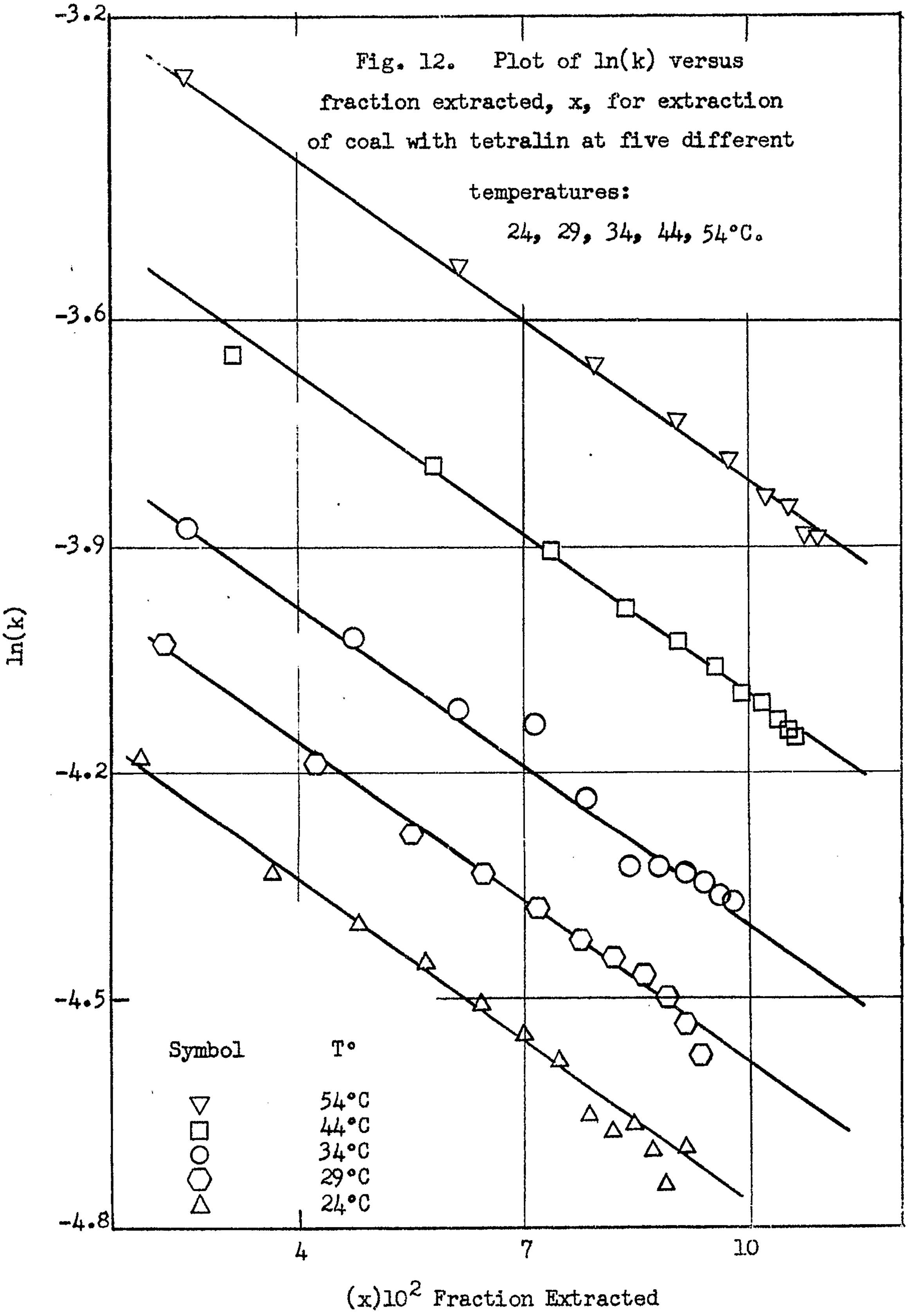

Fig. 12. Plot of ln(k) versus fraction extracted, x, for extraction of coal with tetralin at five different temperatures: 24, 29, 34, 44, 54°C.

$\Delta F_o^{\ddagger}$ is the initial free energy of activation,

T is absolute temperature,

R is gas constant,

t is time.

The above expression upon integration does not give a linear relationship between the logarithm of x and time (t). It predicts a more complex reaction mechanism than a simple first order reaction for the extraction of coal. It appears that the complexity of the coal reacting with the solvent (tetralin) varies with time during the extraction process, and such change in composition corresponds to a different free energy of activation ($\Delta F^{\ddagger}$). Because $\Delta F^{\ddagger}$ is composed of terms for activation enthalpy and activation entropy, a factor, f(x), a concentration term, can be added that might be attributed to either of these components as expressed by the following equation:

$$\Delta F^{\ddagger} = \Delta F_o^{\ddagger} + f(x) = \Delta H_o^{\ddagger} + bx - T\Delta S_o = \Delta F_o^{\ddagger} + bx \qquad (17)$$

or the equation:

$$\Delta F^{\ddagger} = \Delta F_o^{\ddagger} + f(x) = \Delta H_o^{\ddagger} - T(\Delta S_o - bx) = \Delta F_o^{\ddagger} + bTx \qquad (18)$$

By substitution, Equation (16) becomes:

$$\frac{dx}{dt} = (a-x)\,\frac{kT}{h}\,\exp\left(-\frac{\Delta H_o^{\ddagger}}{RT} + \frac{\Delta S_o^{\ddagger}}{R} - \frac{b'x}{RT}\right) \qquad (19)$$

If b'=b then Equation (17) is valid and the contribution is to the enthalpy term; but if b'=bT, the contribution is to the entropy term. A reliable way to determine the temperature dependence of b' is to plot ln(k) versus x for different temperatures (Fig. 12). It was found that the slopes of the lines do not vary with temperature, therefore coefficient for x has to be in the form: $b' = bT$, and it is included in the entropy term, $\Delta S^{\ddagger}$.

From Fig. 12, $\frac{b}{R}$ was found to be 7.2 cal/mole-deg by averaging the slopes of the five straight lines. The value of b calculated was 14.4 ± 0.2 cal/mole-deg. With this value of b, the contribution to entropy would range from a value of zero e.u. when $x=0$ to -1.66 e.u. when $x=x_m$, the maximum yield for the given test conditions. According to Hill's (57) interpretation, the decrease of activation entropy ($\Delta S^{\ddagger}$) with extraction yield is probably a result of the decrease in number of surface sites. Since a change of 4.6 entropy units in the apparent activation entropy corresponds to a change in surface sites availability by roughly a factor of ten, the decrease of 1.66 entropy units in this experiment is, therefore, corresponding to a decrease of about one quarter of the original available surface sites where the extraction is taking place. The changes of activation entropy as a function of extraction yield for the five experimental temperatures are shown as Table 17. The final data on rate constants for the extractions of coal are given in Table 5. By employing Arrhenius' and Eyring's equations, the activation energy is obtained by plotting $\ln(k_o)$ against the reciprocal of test absolute temperature. The k_o's were found for different temperatures by determining the intercepts with the y-axis for the lines shown in Fig. 12 for data plotted in the form $\ln(k)$ versus the fraction of coal extracted, x. From Figure 13 one can find the activation energy for the process, $E_a=6.7$ kcal/mole. By plotting $\ln(k_o/T)$ versus $1/T$, the activation enthalpy and the initial activation entropy were found from Fig. 14 to be 6 kcal/mole and -54.5 e.u. respectively.

Table 5. Final results for solvent extraction of coal with tetralin.

T°K	$(1/T)10^3$	k_{of}	$(k_o/T)_f 10^5$	k_{oI}	$(k_o/T)_I 10^5$	$\ln(k_o)_I$	$\ln(k_o/T)_I$	$\ln(k_o)_f$	$\ln(k_o/T)_f$
297	3.367	0.0172	5.7912	0.01694	5.7037	-4.0788	-9.7735	-4.0635	-9.7583
302	3.311	0.0208	6.8874	0.02148	7.1126	-3.8393	-9.5527	-3.874	-9.5855
307	3.257	0.0246	8.0130	0.02402	7.824	-3.725	-9.4574	-3.705	-9.4329
317	3.155	0.0346	10.9148	0.03548	11.1924	-3.3394	-9.0995	-3.366	-9.1259
327	3.058	0.0482	14.7401	0.04763	14.5657	-3.0448	-8.8355	-3.033	-8.824

E_a = 6.7 kcal/g-mole

$\Delta H_o^{\ddagger}$ = 6.0 kcal/g-mole

f = method of finite differences

I = Integrated form of equation
(see Table 16 in Appendix)