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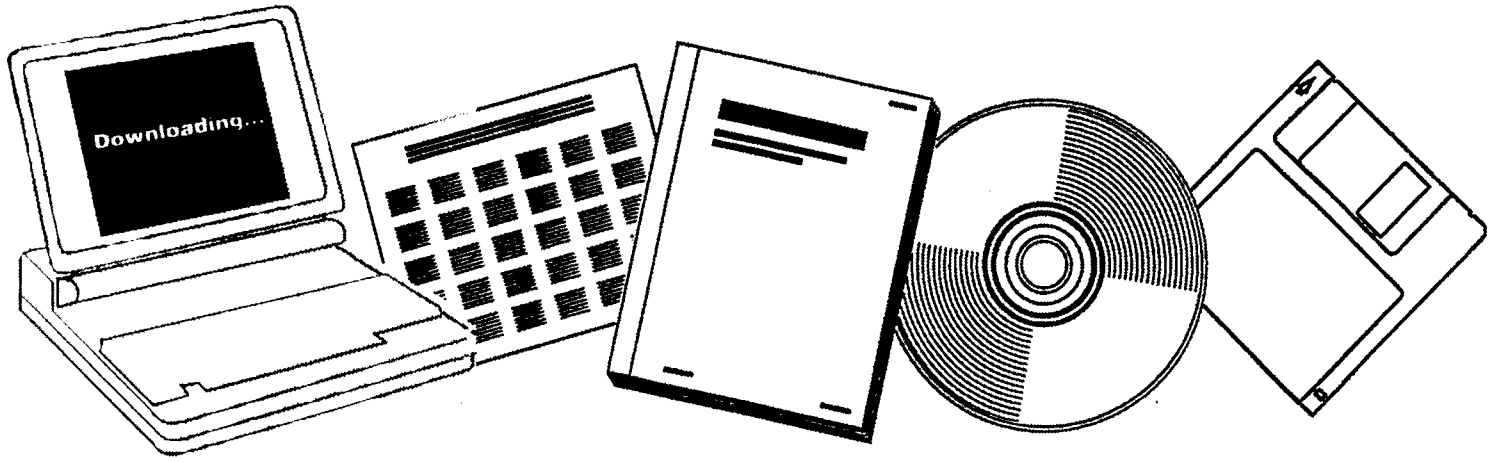
MAY 1970



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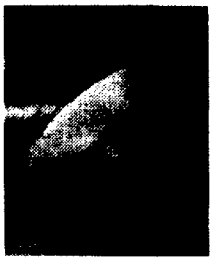

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The objective of Project Western Coal was to determine the convertability of various coals in the Western United States into liquid and gaseous products. This report summarizes the results of 13 different laboratory investigations of coal processing, including flash heating and plasma pyrolysis, hydrogenation processes, solvent extraction, microwave radiation processing, catalytic studies, and others. Many of the detailed results of individual parts of this work have been described previously before various scientific organizations and in technical publications. This report includes a bibliography listing 48 such prior papers based on this work.

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FINAL REPORT

UNIVERSITY OF UTAH

DEPARTMENT OF MINERAL ENGINEERING

AND

OFFICE OF COAL RESEARCH

DEPARTMENT OF INTERIOR

PROJECT WESTERN COAL:

CONVERSION OF COAL INTO LIQUIDS

Project Period: August 25, 1962 - December 24, 1969

Contract No. 14-01-0001-271

Prepared by

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INTRODUCTION

Project Western Coal was initiated in 1962 as a United States Office of Coal Research and State of Utah project to determine the convertability of various coals in the western United States into liquid and gaseous products.

Various techniques were investigated for producing stable hydrocarbons by the introduction of hydrogen atoms into the free radicals produced from heated coal. Stabilizing the initial low molecular weight distillate radicals prior to their polymerization insures a product easily convertable into gasoline and diesel range products and minimizes the quantity of tar, much of which ultimately ends up as char or coke.

Several "levels" or intensity of treatment were investigated. These included plasma pyrolysis, flash heating, thermal pyrolysis, catalytic hydrogenation, solvent extraction and hydrogenation distillation. It was demonstrated that short heating time (less than one second) of coal particles in a system where hydrogen stabilization of the initial product was accomplished quickly gave optimum yields of products readily convertable to the desired products. Total dissolution of the coal can also be accomplished with suitable hydrogen donor solvents but the heavy ends of the liquid produced are very hydrogen deficient. These are difficult to convert to gasoline range hydrocarbons. It was concluded to pursue the hydrogen-distillation technique.

A disperse phase, down-flow free fall reactor was built which met the requirements of short residence time in a hydrogen atmosphere. Various western coals have been treated in the hydrogenation-distillation reactor to determine comparative yields of liquid and gaseous products. The effects of (and optimum ranges of) temperatures, pressure, residence time, catalysts, coal pre-treatment and particle size have been determined. It is now necessary to scale up the reactor size to get engineering data on a semi-continuous unit to determine the economic feasibility of the process.

During the work it has been necessary to develop analytical techniques for characterizing the liquids and gases produced. Gel permeation chromatography, gas liquid chromatography and mass spectrometry as well as normal chemical characterization methods have been used or developed.

A portion of the effort has also been devoted to quantitative studies of the catalysts and conditions required for conversion of the primary distillates into gasoline and diesel oils. These products have been characterized using ASTM procedures.

Fundamental kinetic data have been determined for pyrolysis, solvent extraction and hydrogenation -- on the same coals -- so that comparative reaction rates can be predicted for many temperature and pressure regimes.

The results of the work have been presented as technical papers and publications of various technical societies including the A.C.S., A.I.Ch.E., A.I.M.E. and at Gordon Conferences and International Coal Science Conferences. This final report summarizes the technical findings to date and lists the scientific and engineering publications which have resulted from the work.

Projects I, II(a) and II(b). FLASH HEATING AND PLASMA PYROLYSIS OF COAL

Studies on rapid heating of coal to moderate and high temperatures by making very large amounts of energy available were carried out in these studies. These studies were conducted both to learn more about the coal structure and to investigate the possible economics of producing chemicals or fuels by the unique reaction of flash heating and plasma pyrolysis.

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 auxiliary wiring. The apparatus was assembled in the Fuels Engineering Department 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 flash lamp 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 SRH 555). The plasma torch operated continuously at 6 kw. for periods of up to more than two hours. This torch was patterned after one designed by Stokes and Knipel 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 radiant energy from the flash lamp.

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.

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.

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[2]. 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.

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.

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 plasma 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.

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. Apparently 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 were, 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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1. Stokes, C. S., and W. W. Knipe, Ind. Eng. Chem., 52, 287 (1960).

2. Smith, M. L., and K. W. Stinson, "Fuels and Combustion," McGraw-Hill, New York (1952).

Projects III(a), V(c), V. COAL PYROLYSIS STUDIES

Introduction

Coal pyrolysis studies have been conducted under constant temperature conditions utilizing a Utah high-volatile bituminous coal. The first study[1] utilized a quartz spring balance and covered the temperature range 409° to 497°C. The second study[2] also utilized the quartz spring balance and expanded the temperature range, covering the range 281° to 652°C. The aim of the second study was to determine whether the kinetics observed over the narrow temperature range also applied at the lower and higher temperatures. A third study[3] was conducted utilizing an electrobalance and very small samples, thereby permitting rapid attainment of reacting temperature by the sample as well as continuous data recording. This study was conducted to determine whether the observed kinetics extended to short times approaching the beginning of the pyrolysis reaction, since product evolution is very rapid in the first few minutes, and the model must also explain this product evolution. This study utilized a Colorado high-volatile bituminous coal.

Experimental Procedure

The equipment used in the first two studies consisted of a vertical tube-type furnace with facility for maintaining constant temperature within ± 3°C. In the first study a stream of nitrogen gas at constant flow rate was admitted at the top of the furnace and flowed downward over the sample. In the second study helium was used for this purpose. The coal samples used contained about 48% volatile matter. For the first study, -40 + 60 mesh particles were used; for the second study the particles were -400 mesh. Sample size for both studies was about one gram. In each case zero time was taken when the sample, suspended on a quartz spring, was lowered into the preheated reaction zone. The weight loss was observed by measuring the deflection of the quartz spring with the aid of a cathetometer.

The equipment used in the third study consisted of a Fisher Thermogravimetric Analysis Accessory Model 120, a Fisher Linear Temperature Programmer Model 360, with provision for raising the preheated reaction chamber around the sample suspended from a Cahn Electrobalance. Samples of approximately 9 mg were used. Weight losses as measured by the electrobalance were continuously recorded. The time required for the sample to reach constant temperature was generally less than one minute in this study.

Results and Discussion

Typical fractional weight loss-time curves for the first and second studies are shown in Figure 1. Typical curves from the third study, for short times, are shown in Figure 2.

If it is assumed that the average molecular weight of the products remains essentially constant during the pyrolysis process, weights may be used instead of mole fractions in the kinetic equations. It was observed that the data in all three studies fit second order rate expressions from the beginning throughout most of the product evolution, with a transition to first order late in the evolution process. In general the percentage of the total volatile product evolved under second order conditions varied from about 65 per cent at the lower temperatures to about 96 per cent at the higher temperatures investigated. However, the slope of the straight line produced on a plot of the integrated form of the rate equation changed as the temperature increased. The following values were consequently obtained for the enthalpies of activation, $\Delta H^{\ddagger}$, and entropies of activation, $\Delta S^{\ddagger}$, for the Utah high-volatile bituminous coal for the various temperature ranges as indicated. (The reader is referred to the original technical reports for a complete presentation of the data).

Temperature Range	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, entropy units
317-342°C	19.5	-44.3
359-409°C	31.1	-26.3
409-497°C	35.6	-12.0
500-652°C	8.4	-62.8

The Colorado high-volatile bituminous coal pyrolyzed with the use of the electrobalance yielded values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of 26.7 kcal/mole and -16.6 entropy units, respectively, over the temperature range 408° to 491°C.

All of the above values for $\Delta H^{\ddagger}$ indicate various, but probably different, chemical reactions are rate controlling, except the value of 8.4 kcal/mole obtained for the temperature range 500-652°C. This value indicates some physical factor as rate controlling in the product evolution process. It seems probable that with the extremely rapid reactions at the higher temperatures, diffusion of the product gases through the porous structure of the coal is slow by comparison and becomes rate controlling.

The initial decomposition in coal pyrolysis probably involves thermal rupture of bonds in the links joining adjacent aromatic clusters[4]. In thermal cracking of hydrocarbons in the petroleum industry, the decomposition reactions become appreciable at 350°C. Studies of hydrocarbon cracking processes have demonstrated a tendency for the rupture of an aliphatic chain connected to an aromatic ring to occur at the junction of the aliphatic chain and the ring. A cleavage of this type produces two free radicals as indicated by step (1) in the sequence below.

In order for a fragment thus formed to evolve as volatile material it must be stabilized either through a rearrangement of atoms within the

fragment or through collision with another fragment or molecule. Such fragments or molecules may be produced by thermal cracking processes as indicated by steps 2-a and 2-b below.

Considering the high degree of unsaturation occurring in coal, as indicated by the low hydrogen-carbon ratio, it is likely that collision of particles accounts for a major proportion of stabilization, as indicated in steps 3-a, 3-b and 4. These reactions involve migration of the fragments, orientation and finally reaction. The coal manifests a degree of plasticity throughout the time of the reactions of this region, which facilitates these operations. The vapor pressure of the fragment after stabilization determines whether it escapes as volatile matter or remains as part of the char.

The sequence of events may thus be represented:

1. $\text{(M)}\text{—}(CH_2)_x\text{—}\text{(N)}\text{—R} \longrightarrow \text{(M)}^- + {}^-(CH_2)_x\text{—}\text{(N)}\text{—R}$

2-a. $\text{R—(P)—}(CH_2)_y CH_3 \longrightarrow \text{R—(P)}^- + {}^-(CH_2)_y CH_3$

2-b. $\text{R—(N)—}(CH_2)^-_x \longrightarrow \text{R—(N)}^- + (CH_2)_x$ where $x > 1$

3-a. $\text{(M)}^- + {}^-(CH_2)_y CH_3 \longrightarrow \text{(M)—}(CH_2)_y CH_3$

3-b. $\text{(M)}^- + {}^-(CH_2)_y CH_3 \longrightarrow \text{(M)—H} + (CH_2)_{y+1}$ (e.g. $CH_2{=}CH\text{-}CH_3$)

4. $\text{(M)}^- + {}^-\text{(P)—R} \longrightarrow \text{(M)-(P)—R}$

The velocity of thermal decomposition reactions in hydrocarbons has been observed to increase very rapidly with temperature, doubling the rate for each 10°C temperature increase in the temperature range 350-450°C. As the veolocities of reactions (1) and (2) of the above sequence increase, the reactions of step (3) become more important in the determination of the overall rate. (Reactions involving migration and orientation would not increase as rapidly with temperature as purely decomposition reactions.) Hence the overall reaction becomes second order and reactions of the type depicted in step (3) become rate determining.

In purely bimolecular reactions, the value of the frequency factor "A" in the Arrhenius equation has been observed to assume values of 10^{10} to 10^{11}, while unimolecular reactions yield values of "A" of 10^{13} to 10^{14}. The value of "A" as determined from the intercept of an Arrhenius plot, for the second order region, is 10^{11}, indicating a bimolecular or second order reaction.

The process of the first order region was characterized by an activation energy of 5.36 kcal/mole, which is lower than observed for chemical reactions, but indicative of some physical process. Shapatina observed a first order region with activation energy of 5.3 kcal/mole and Stone observed a first order region with activation energy of 6.7 kcal/mole. The

value of the frequency factor "A", as determined from an Arrhenius plot for this region, is 0.54. This great departure from the values observed above seems to indicate a process other than a unimolecular or first order chemical reaction.

Inasmuch as the reactions of the second order region occur throughout the mass of the coal, species produced with sufficient vapor pressure to escape as volatile matter must diffuse to the surface in order to escape. The disappearance of the plastic state, with the associated fusion of the char, greatly restricts this diffusion and escape. As the mass again becomes solid, the volatile matter may escape only through the existing channels, at a rate determined by the length, cross-sectional areas and structures of these diffusion paths, and by the pressures within the pores. It is believed that the first order region under consideration is the manifestation of a diffusion-controlled process.

References

1. N. J. Kertamus, "Pyrolysis Kinetics of a Utah Coal with Discussion of Lithium Reduction and Batch Hydrogenation," Technical Report, Department of Interior, Office of Coal Research, Contract Number 14-01-0001-271, July (1964).

2. M. M. El-Mogazi, W. H. Wiser, and G. R. Hill, "Kinetics of Pyrolysis of High Volatile Bituminous Coal," Technical Report, Department of Interior, Office of Coal Research, Contract Number 14-01-0001-271, February (1967).

3. A. A. Elmowafi and W. H. Wiser, "Pyrolysis Kinetics of High-Volatile Bituminous Colorado Coal," Technical Report, Department of Interior, Office of Coal Research, Contract Number 14-01-0001-271, September (1969).

4. W. H. Wiser, G. R. Hill, and N. J. Kertamus, "Kinetic Study of the Pyrolysis of a High Volatile Bituminous Coal," I. and E.C. Process Design and Process Development 6, 133 (1967).

Project III(b). GAS CHROMATOGRAPHY

This project involved the setting up and operation of a F & M Scientific Model 720 Gas Chromatograph which had been purchased with OCR funds. This instrument from the date of purchase to the end of the contract served as one of the basic analytical tools for qualitative and quantitative analysis of solids, liquids and gases. The initial operation, calibration and some study of the polymerization of liquid products from coal comprised this project from February 1963 to August 1963. After this date no work was done nor were funds expended on these activities except in connection and as reported with other projects. The research on polymerization of coal-derived liquids was conducted to ascertain the variables

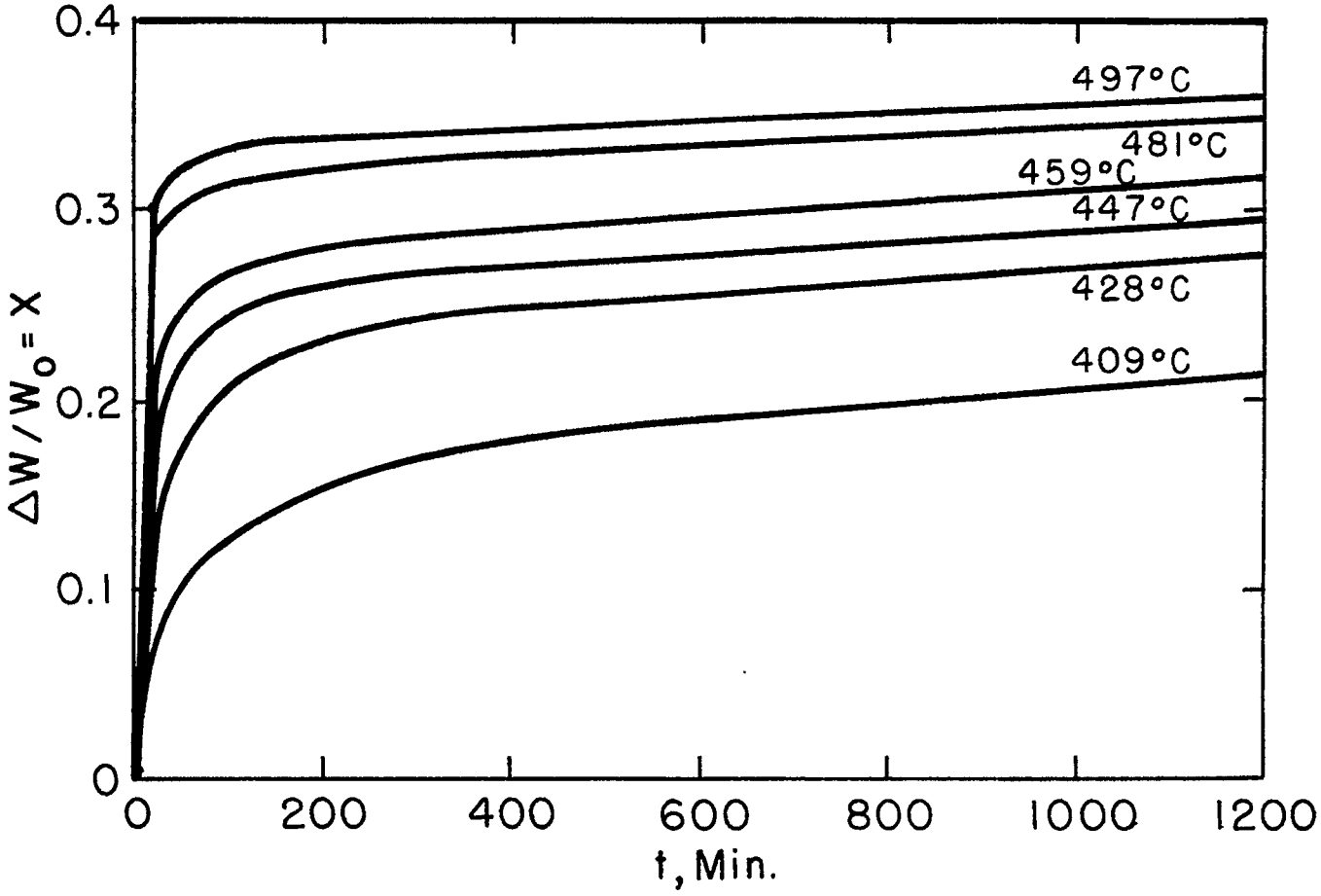

Figure 1. Fractional Weight Loss-Time Curves.

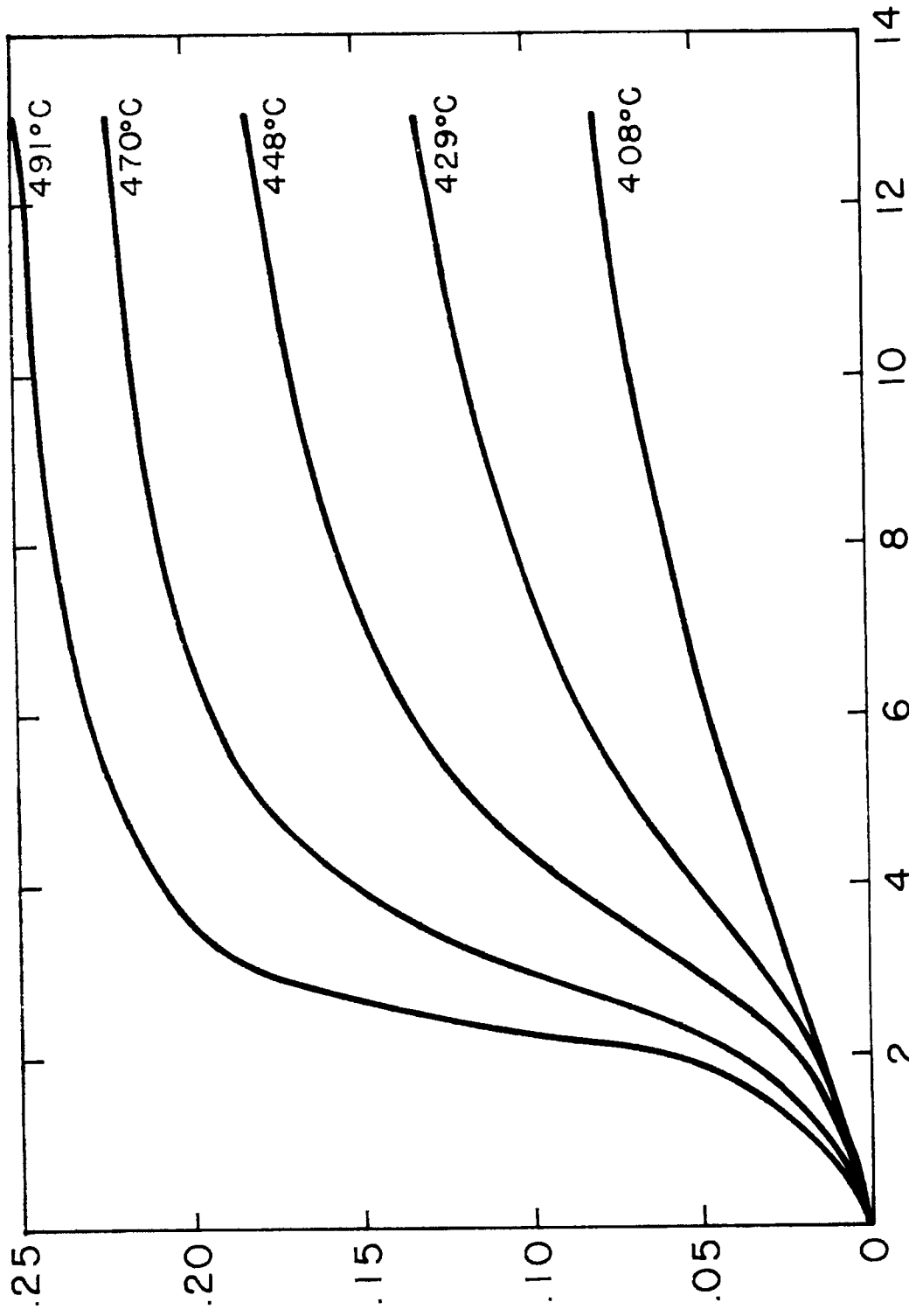

Figure 2. Fractional Weight Loss–Time Curves of High-Volatile Bituminous Colorado Coal.

which affect this important reaction. Briefly, the reactions involve darkening of the liquid from a transparent or light yellow cast through orange, brown and finally to black. This color change was accompanied by an increase in viscosity and a large increase in pour point. Observations of liquids from oil shale and petroleum distillation often exhibit similar reactions to a more or less degree.

To study the reaction an apparatus was constructed to control the gas phase in contact with the liquid sample. Other variables studied were temperature, light energy, and free radical concentration.

Results of this brief study showed that high temperature and oxygen influence the reaction rate and extent. Free radicals were not detected by Electron Spin resonance analysis, but this did not eliminate the possibility of a free radical mechanism for the reaction.

Although this work was not concluded with definite data accumulated regarding activation energy, rate, or variable coefficients the reactions are very important. Liquid products from coal which may be apparently very valuable can be drastically reduced in value by polymerization. These reactions should receive additional study.

Project III(c). CATALYTIC HYDROGENATION OF COAL TAR

Introduction

This project was undertaken to determine the variables and their effects governing the hydrogenation of high temperature coal tar to liquid fuels, primarily gasoline. The coal tar used as reactant was obtained by carbonization of a Utah high volatile bituminous coal at 1200°C. The carbonization step was carried out by United States Fuel Company of Salt Lake City, Utah. The effects of temperature (350-475°C), hydrogen pressure (500-3000 psig), contact time (up to twenty-eight hours), and catalyst composition were studied. More extensive tests and analyses were carried out for conditions which appeared to be best for producing highest yields and quality of gasoline.

Materials and Procedure

The coal tar sample was a dark brown to black semisolid material which contained water. After removal of the water the tar had properties as indicated in the following table (Table I).

The fraction boiling below 230°C was arbitrarily designated as the gasoline fraction.

Hydrogen was taken from a cylinder with a maximum pressure of 2300 psi.

TABLE I

EFFECT OF TEMPERATURE ON PRODUCT DISTRIBUTION AT 3000 PSI

Temperature, °C	350	375	400	425	450	375
Reaction time, hrs.	26	20	18	14	12	10
Product distribution, wt. %						
Gasoline	23	33	46	56	65	77
Middle oil	50	46	34.5	26	17.5	4
Gas	nil	1	2.5	3	4.5	6
Residue	27	20	17	15	13	13
Tar acids	15	2	nil	--	--	--
Tar bases	2	1	nil	--	--	--
Hydrocarbon types in neutral oil boiling up to 230°C, vol. %						
Saturates	71	73	74	79	80	82
Olefins	2	2	2	1	1	1
Aromatics	27	25	24	20	19	17

The catalyst used for this study was molybdenum trioxide (MoO_3) powder, -200 mesh, AR grade obtained from Mallincrodt Chemical Company. The catalyst powder had a surface area of 190 square meters per gram.

The reactions were conducted in a 1 liter magnedrive autoclave which was equipped with a water quenching system, external heater, stirring control and liquid and gas sample lines. Tar sample (200 grams) and catalyst were weighed and placed into a glass liner which was inserted into the autoclave. The autoclave was evacuated by vacuum pump and then pressurized with hydrogen. After the reaction was conducted the system was quenched with cool water, the gases measured through a gas meter and the liquids removed for distillation.

For the kinetic data points samples of liquid were removed periodically during the reaction to determine the gasoline content. The samples taken were small (approximately 4 grams) and required microdistillation. This

was done to avoid changes in pressure or other conditions of the experiment.

Results and Discussion

The preliminary experiments conducted to determine optimum conditions for production of gasoline are summarized in Table II.

TABLE II

EFFECT OF REACTION VARIABLES ON GASOLINE PRODUCTION

Variable	Range Studied	Gasoline Yield Range	Comments
Amount of MoO_3 Catalyst Used	0-8%	5% - 48%	Gasoline yield increased linearly with % catalyst to 6% then tapered off somewhat.
Stirring speed	0-2000 r.p.m.	8.5%-41%	Increased stirring was effective to 1500 r.p.m.
Hydrogen Pressure	0-3000 p.s.i.	7% - 65%	Increase in gasoline with increasing P_{H_2} evident throughout range studied.
Temperature (@ 3000 p.s.i.)	350-475°C	23 - 77%	Linear increase in gasoline yield with temperature throughout the range studied.

Effects of the variables studied are shown graphically in Figures 1, 2, 3, and 4. The highest yield of gasoline obtained was 77% at 475°C, 3000 p.s.i. (hydrogen) with 5% MoO_3 catalyst. The reaction took 10 hours for complete reaction. The highest quality gasoline, containing 60% aromatics, was obtained in a yield of 47% at 450°C with P_{H_2} of 2500 p.s.i.

Experiments to determine the kinetic data for hydrogenation of the coal tar to gasoline were conducted at 350°, 375°, 400°, 425°, 450° and 475°C. The overall process data were fit very well to a first order rate equation. The differential equation applied to the data was:

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

where: x = fraction of tar converted to gasoline at time, t
t = reaction time, minutes
a = maximum value of x at any particular temperature

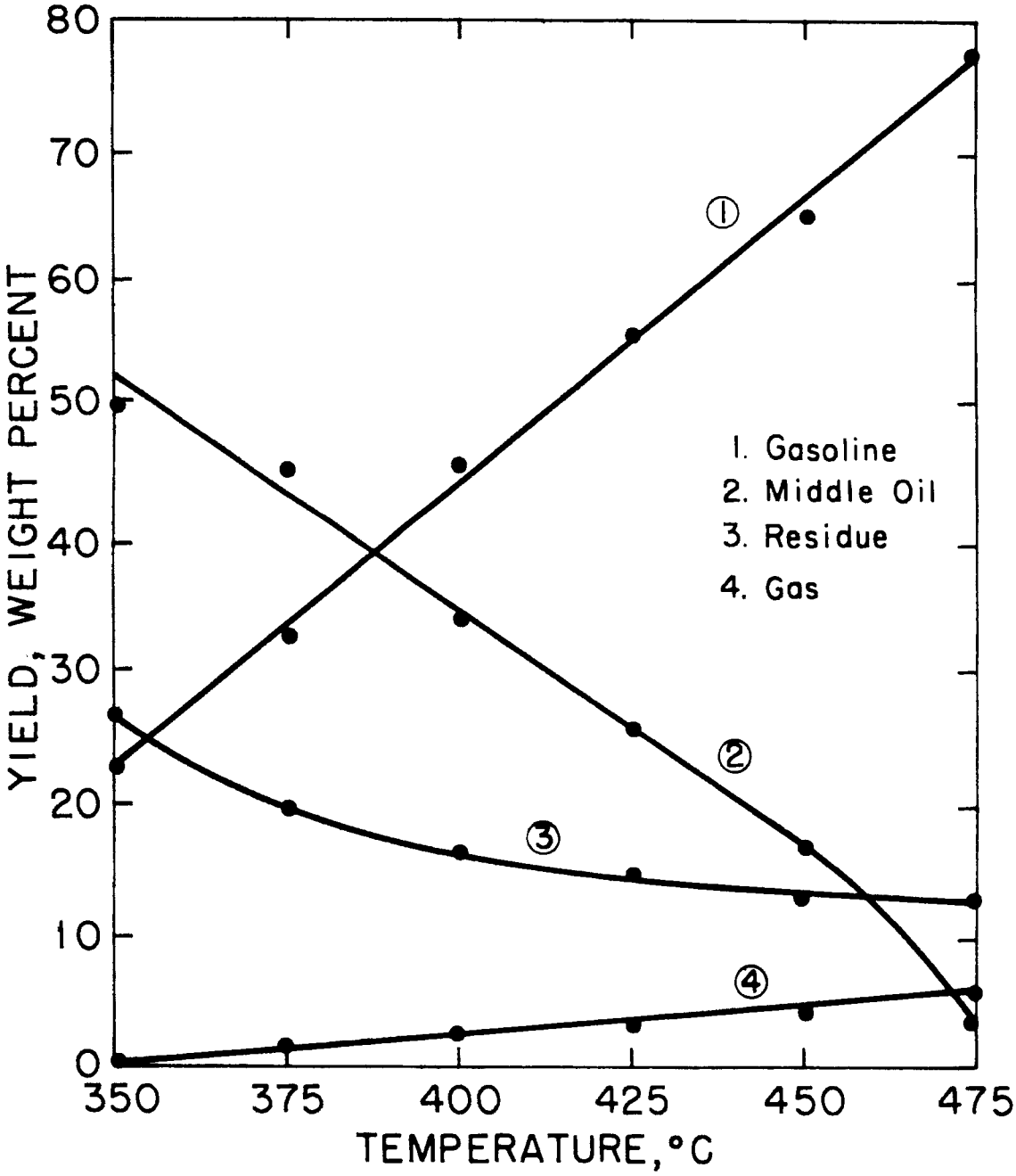

Figure 1. Effect of temperature on product distribution from coal tar hyrogenation.

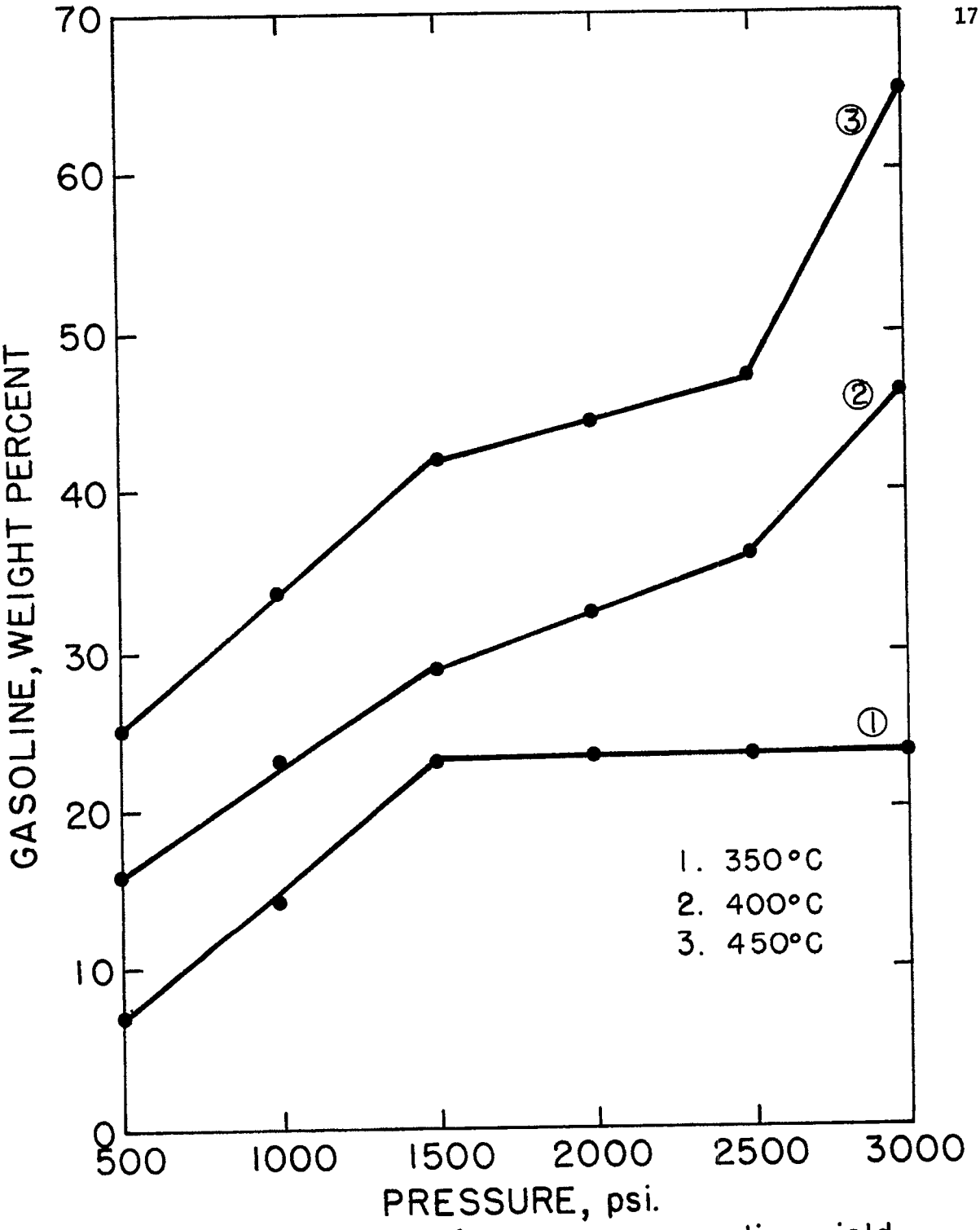

Figure 2. Effect of pressure on gasoline yield from coal tar hydrogenation.

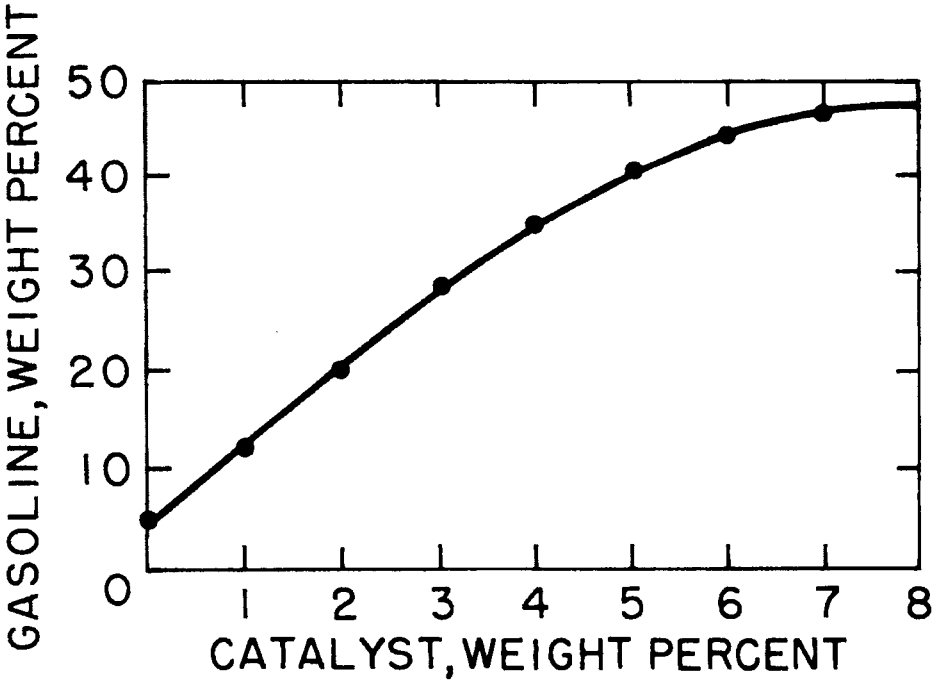

Figure 3. Effect of catalyst amount on gasoline yield from coal tar hydrogenation.

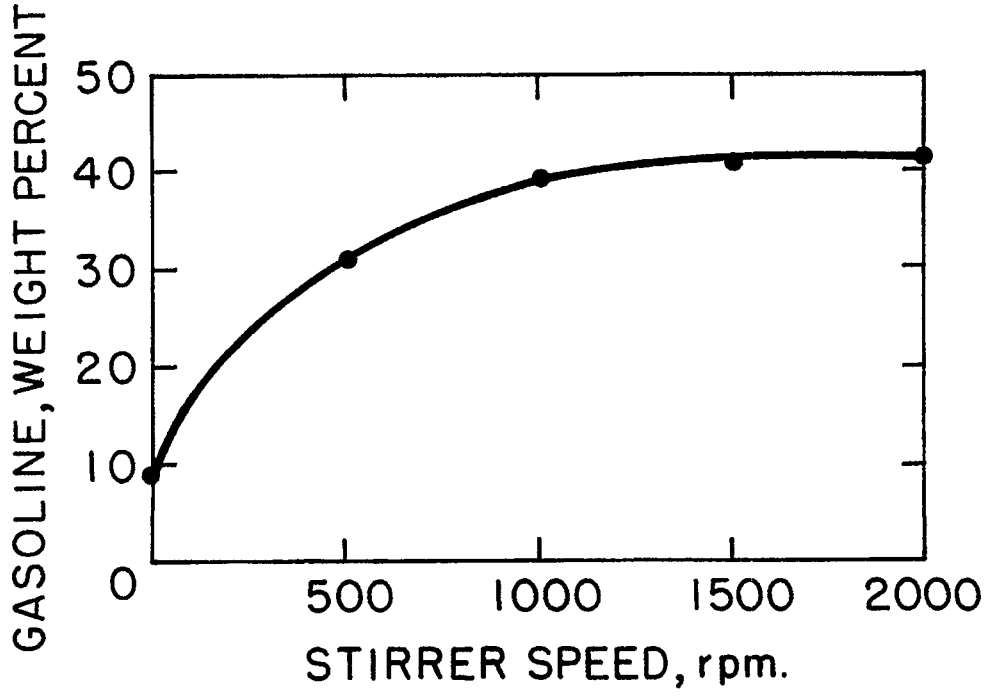

Figure 4. Effect of stirring on gasoline yield from coal tar hydrogenation.

k = reaction velocity constant

Integration of the differential equation and evaluating integration constant yields:

$$\ln \frac{a}{a-x} = kt$$

Plots of this equation are shown in Figure 5 for the temperature range studied.

The specific rate constant for the hydrogenation reaction was assumed to be of the form

$$k = \kappa \frac{k_b T}{h} \exp \left(\frac{-\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R} \right)$$

where: κ = transmission coefficient (usually near 1.0)
k_b = Boltzman constant, 1.38×10^{-16} erg/degree
h = Planck constant, 6.627×10^{-27} erg seconds
T = absolute temperature (°K)
$\Delta H^{\ddagger}$ = enthalpy of activation (kilocalories pere mole)
$\Delta S^{\ddagger}$ = entropy of activation (calories per mole-degree)

Using the above equation $\ln \frac{k}{T}$ versus $\frac{1}{T}$ were plotted and the following values obtained for the reaction:

$\Delta H^{\ddagger}$ = 10.5 kilocalories/mole

$\Delta S^{\ddagger}$ = -57 entropy units

Summary of Results

Hydrogenation of the high temperature tar was affected by pressure, temperature, catalyst concentration, and stirring speed. At low stirring speed some diffusion control is in effect but is eliminated above 1500 r.p.m.

Temperature, catalyst concentration, and pressure increases enhance gasoline production throughout the ranges studied. Experiments were conducted using raw tar containing 14% gasoline as feed and topped tar (0% gasoline). No differences were observed for the different tar feeds. Some experiments were carried out under low hydrogen pressure 0-500 p.s.i. but with the same total pressure ($P_{H_2} + P_{He}$ = 3000 p.s.i.). At P_{H_2} = 200 p.s.i. the rate of reaction was proportional to the square root of the hydrogen pressure. As the hydrogen pressure increases the rate is less dependent on it.

Hydrogenation of tar produced gasoline, (B.p. < 230°C) gas, middle oil (B.p. 230-345°C) and a residue (B.p. > 345°C). The gas produced was composed mostly of methane with small amounts of ethane, carbon dioxide, propane, hydrogen sulfide and ammonia. Representative data are given in Table III.

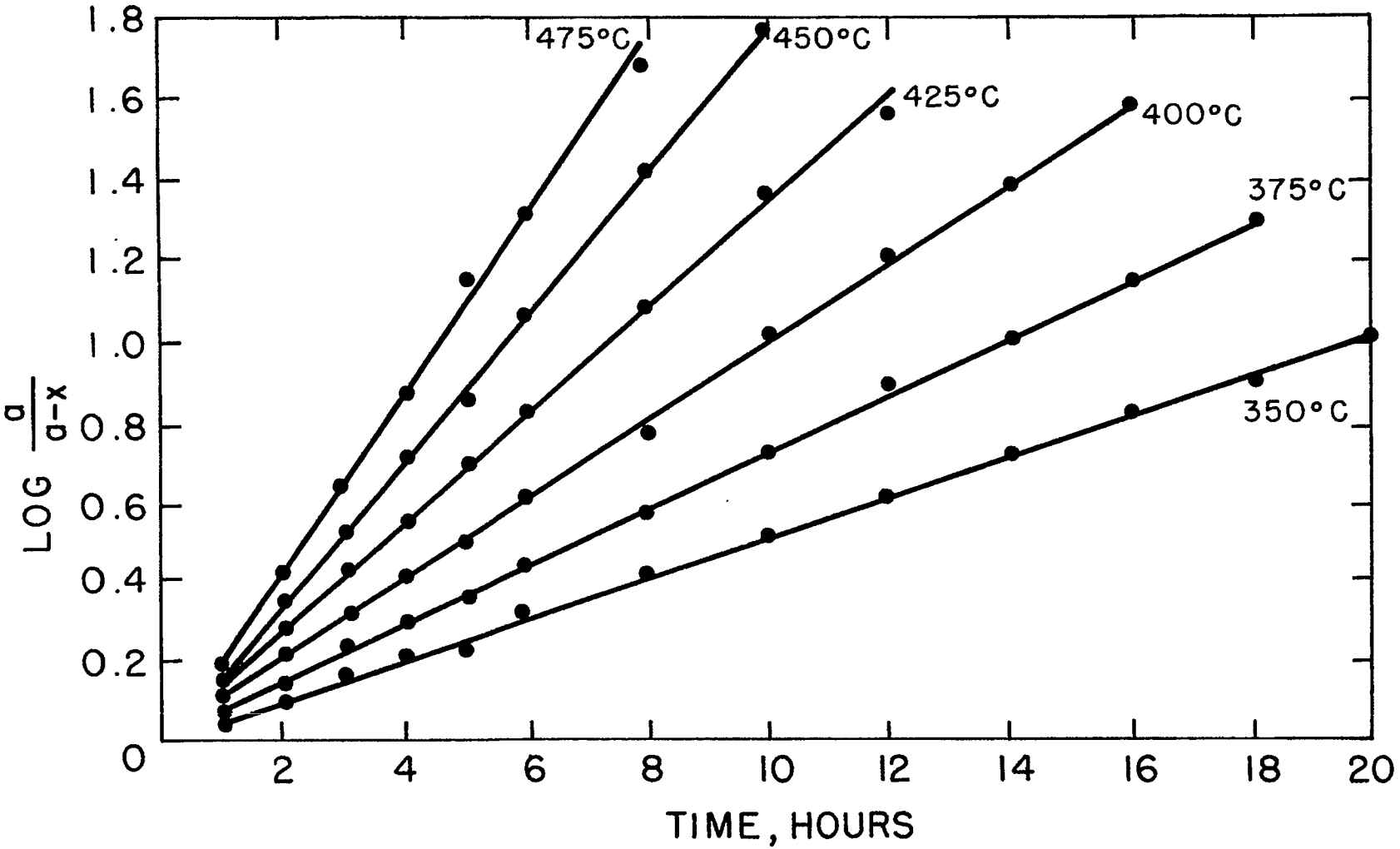

Figure 5. Plot of first order equation.

TABLE III

PROPERTIES OF THE COAL TAR

Sp. gr., 25°C	1.0426
Elements:	WT. %
Carbon	84.9
Hydrogen	9.3
Oxygen	4.1
Nitrogen	0.8
Sulfur	1.1
Distillation data:	°C
I.B.P.	180
14 wt. %	230
50 wt. %	325
55 wt. %	345
Residue	45 wt. %
Hydrocarbon types in neutral fraction 180° to 345°C:	VOL. %
Saturates	20
Olefins	15
Aromatics	65

Conclusion

Hydrogenation of high temperature tar is effective in producing gasoline in yields up to 77% at 475°C, 3000 p.s.i. hydrogen pressure with 5% molybdenum trioxide catalyst for 10 hours. Kinetic studies indicate that three principal types of reactions occur:

hydrocracking of large molecules

hydrogenation of olefins and aromatics

hydro-removal of sulfur, oxygen and nitrogen

These reactions comprise the reactions responsible for the formation of the final products.

The reactions studied were complex and involved many reactions and equilibria. No definite mechanism was deduced from the results. However, from the overall kinetics, the composition of products obtained and other

dependencies of the process the following types of reactions appear to best represent the general reaction sequence:

Cracking:

$$R_1 - R_2 \rightarrow R_1^{\cdot} + R_2^{\cdot}$$

$$R_3H_2C - XR_4 \rightarrow R_3H_2C^{\cdot} + R_4X^{\cdot}$$

Dissociation:

$$R_4X^{\cdot} + H_2^{\cdot} + H \rightarrow R_4H + H_2S \text{ or } NH_3 \text{ or } H_2O$$

where "R" represents a hydrocarbon radical or hydrogen atom and "X" represents sulfur, nitrogen or oxygen.

The kinetic data indicate that the most likely rate-controlling step in the process is adsorption of the reactant molecules on the catalyst surface. The value of the activation energy further suggests that the adsorption taking place is chemisorption.

Project III(c). BATCH HYDROGENATION-DISTILLATION STUDIES

Introduction

Coal is a highly aromatic, hydrogen-deficient hydrocarbon material. To convert it to liquid products resembling petroleum significant quantities of hydrogen must be added. This cannot be effectively achieved without the aid of a catalyst. Temperature, hydrogen pressure and reaction time are also important parameters. All of these parameters have been investigated relative to hydrogenation of coal from Spring Canyon Mine, Utah; then certain selected values of these parameters have been applied to five other bituminous coals, namely Coal Basin, North Thompson Creek and Wellington from Colorado, Gerland from Oklahoma, and Rock Springs from Wyoming.

The catalysts investigated included ammonium molybdate, cobalt molybdate on alumina, nickel tungsten sulfide on alumina, iodine, zinc chloride, stannous chloride, zinc bromide and zinc iodide. Temperatures from 350 to 500°C were investigated.

Experimental Procedure

The equipment[1] consisted of a one-liter rocker-type autoclave equipped with electric heater, temperature controller, variable transformer, pressure recorder, and a vacuum pump. Provision was made for admission or release of gas while the reactor was at operating temperature and pressure. A motor-driven injection pump with a screw feed permitted injection of the coal-oil slurry after the reactor was at operating temperature and pressure,

thus avoiding long times for bringing the sample to the desired operating temperature.

The catalyst was dissolved in mildly acidic water then impregnated upon the surface of the coal particles. After drying, the coal was mixed with oil in a predetermined ratio to form a slurry for injection into the preheated reactor. The time required for injection was two to three minutes, producing a reactor temperature drop of 5 to 10°C only. Approximately three minutes were then required to attain temperature stabilization. Upon completion of the reaction, the reactor was quenched with cold water, requiring about 20 minutes to reach room temperature.

Gaseous products were analyzed with a gas chromatograph and a mass spectrometer. The liquid and solid products were extracted in a soxhlet apparatus at 50°C, using benzene as solvent.

Results and Discussion

Typical time-yield curves showing total conversion to liquid and gaseous products are shown in Figure 1. These yields are for Spring Canyon Coal of Utah. The maximum conversion, obtained at 500°C, with ammonium molybdate catalyst and 1500 psi hydrogen pressure, was 82.0 percent. The maximum liquid yield under these conditions was 49.9 percent.

The data fit a second order rate equation over most of the range of product yield at all temperatures, as illustrated in Figure 2 for the higher temperatures. The activation enthalpy for the second order region was observed to be 38.6 kcal per mole, with an entropy of activation of -17.0 entropy units. This indicates that chemical reactions are rate controlling. The process is believed to be first order with respect to concentration of unreacted coal and first order with respect to hydrogen concentration.

The second order reaction is followed by a first order region with activation enthalpy of 9.5 kcal per mole and activation entropy of -55.9 e.u. This region occurs when the pores have been enlarged by the reaction processes permitting an excess quantity of hydrogen in the reaction zone. Hence the reaction is first order with respect to unreacted coal but zero order with respect to hydrogen.

Considering total conversion as the criterion for catalyst activity, the order of activity for the catalysts investigated is as follows: ammonium molybdate > cobalt molybdate > zinc chloride > stannous chloride > zinc bromide > zinc iodide > nickel tungsten sulfide > iodine.

The effect of catalyst concentration on yield of the various products is shown in Figure 3.

The increase in total conversion with temperature is reflected in Figure 1. The effect of temperature upon yield of various gaseous hydrocarbons is shown in Figure 4.

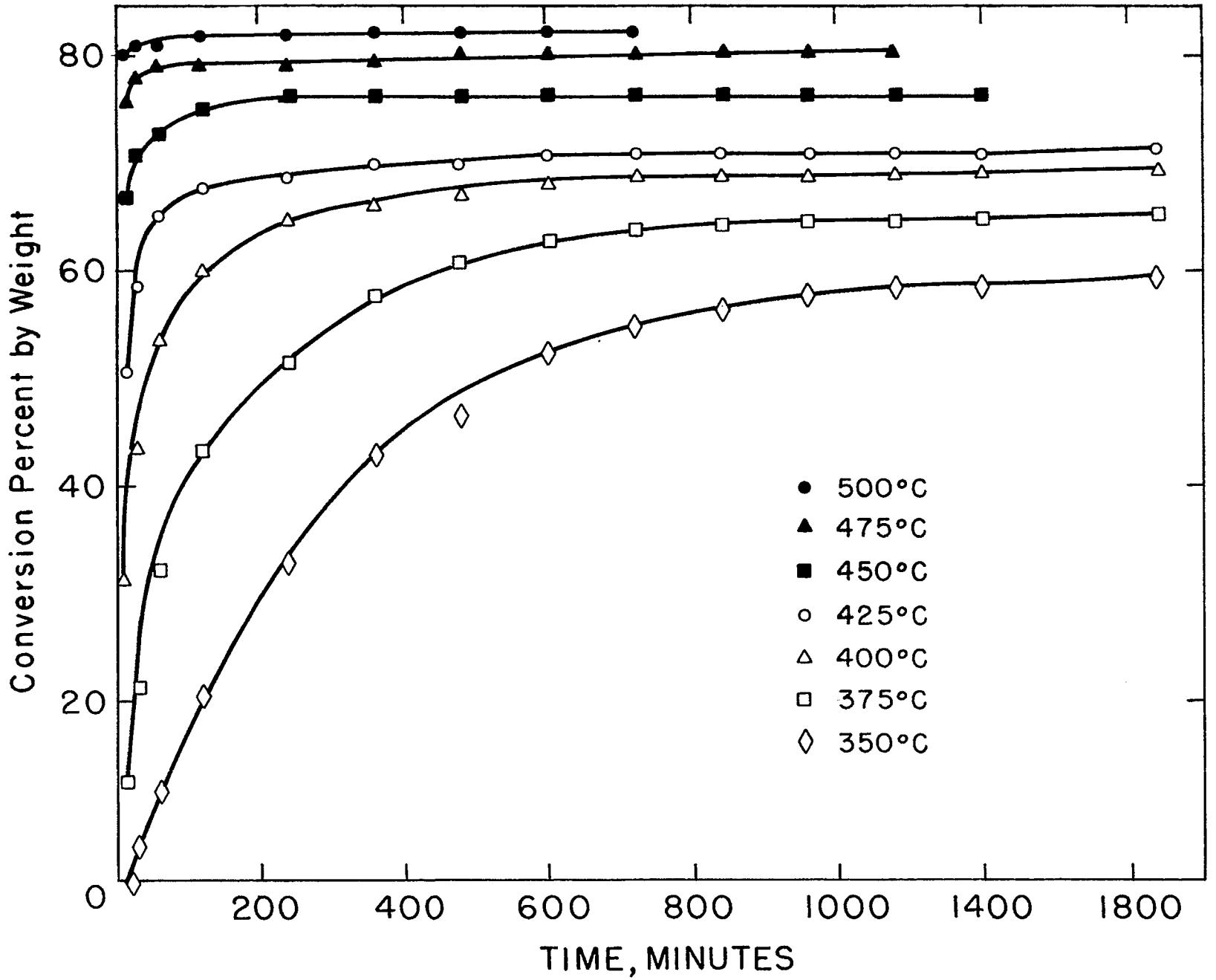

Figure 1. Conversion-time curve of Spring Canyon Coal of Utah.

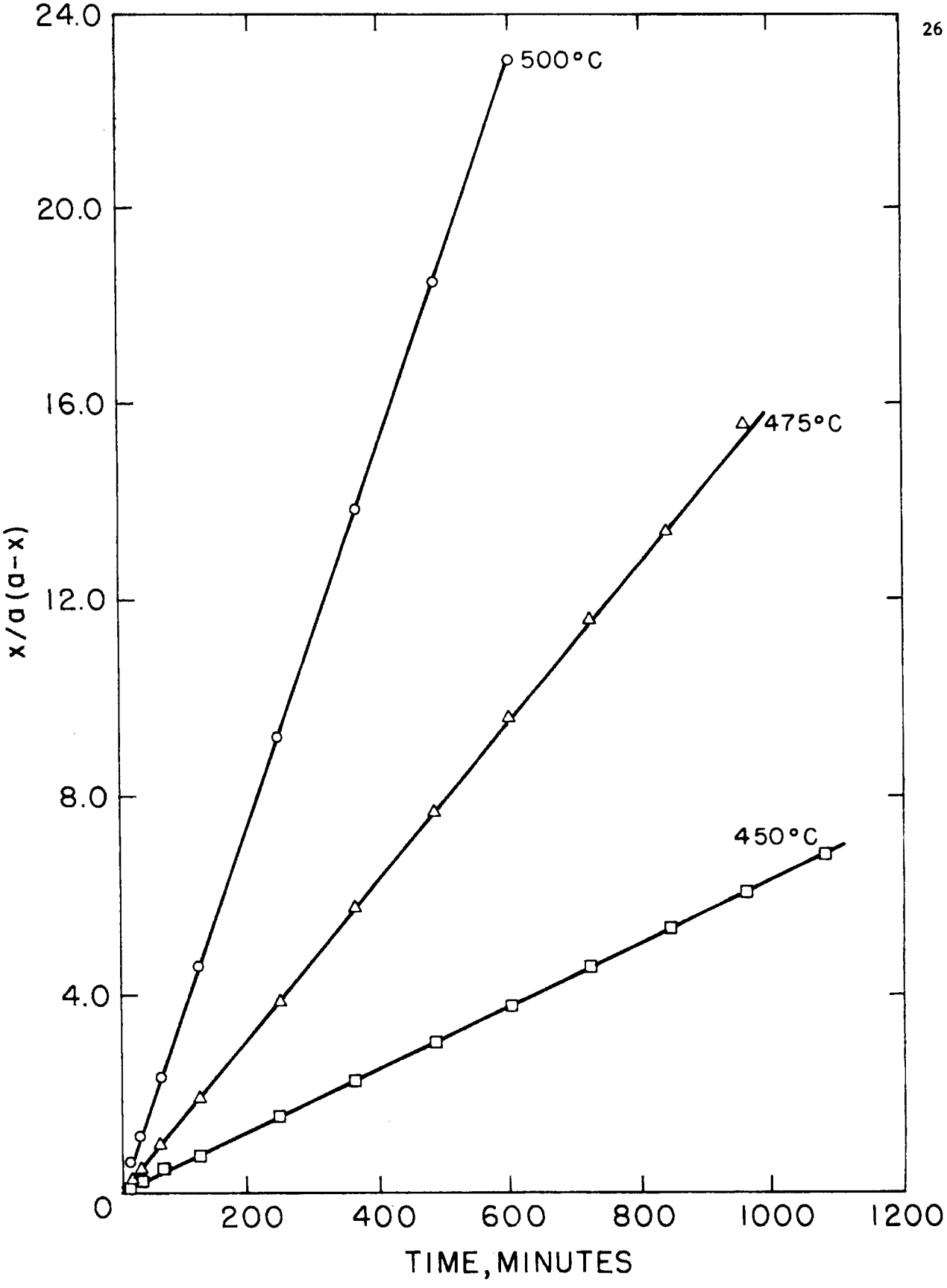

Figure 2. Plot of the second order equation between 450°C and 500°C.

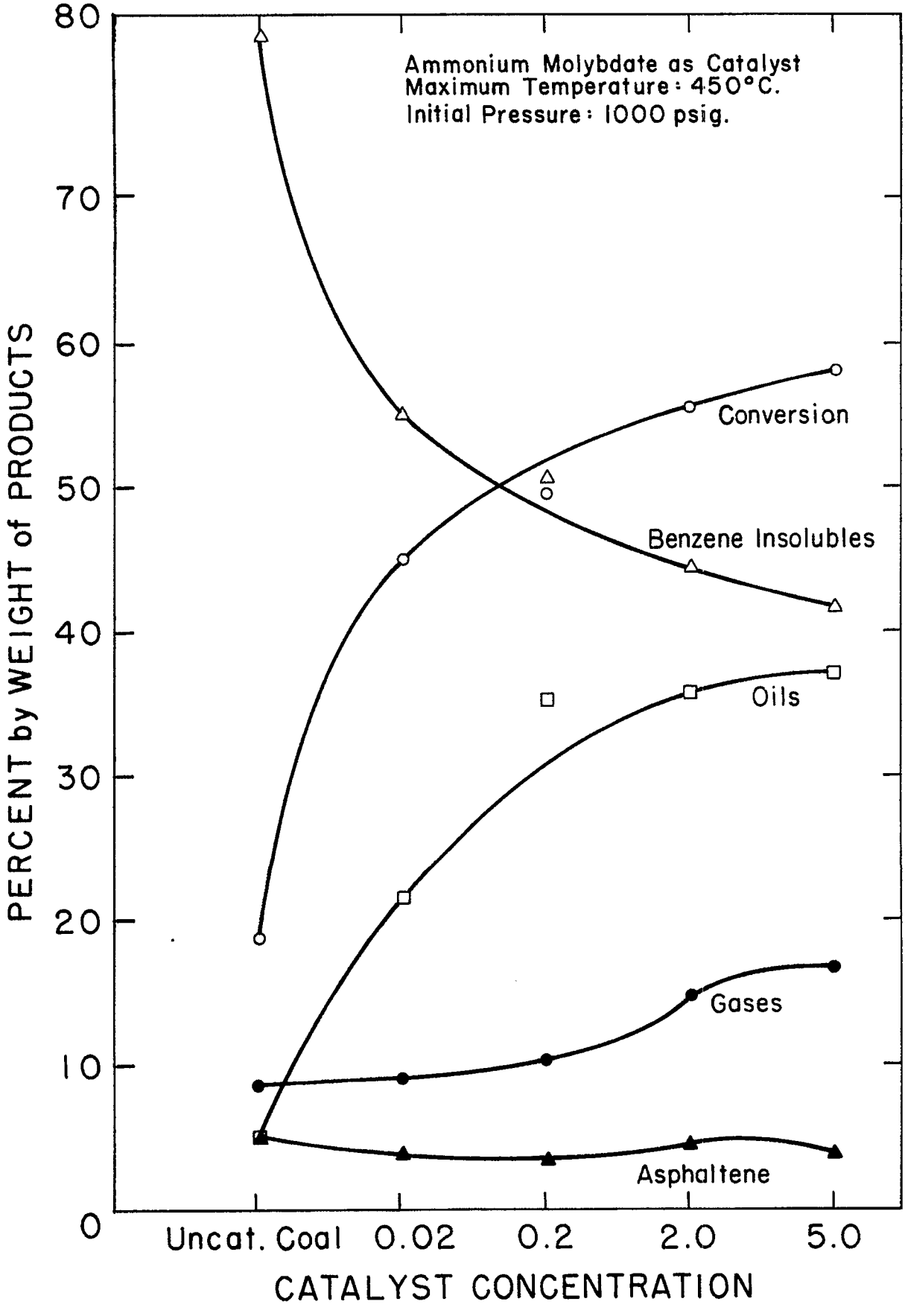

Figure 3. Effect of catalyst concentration on batch hydrogenation of Spring Canyon coal of Utah.

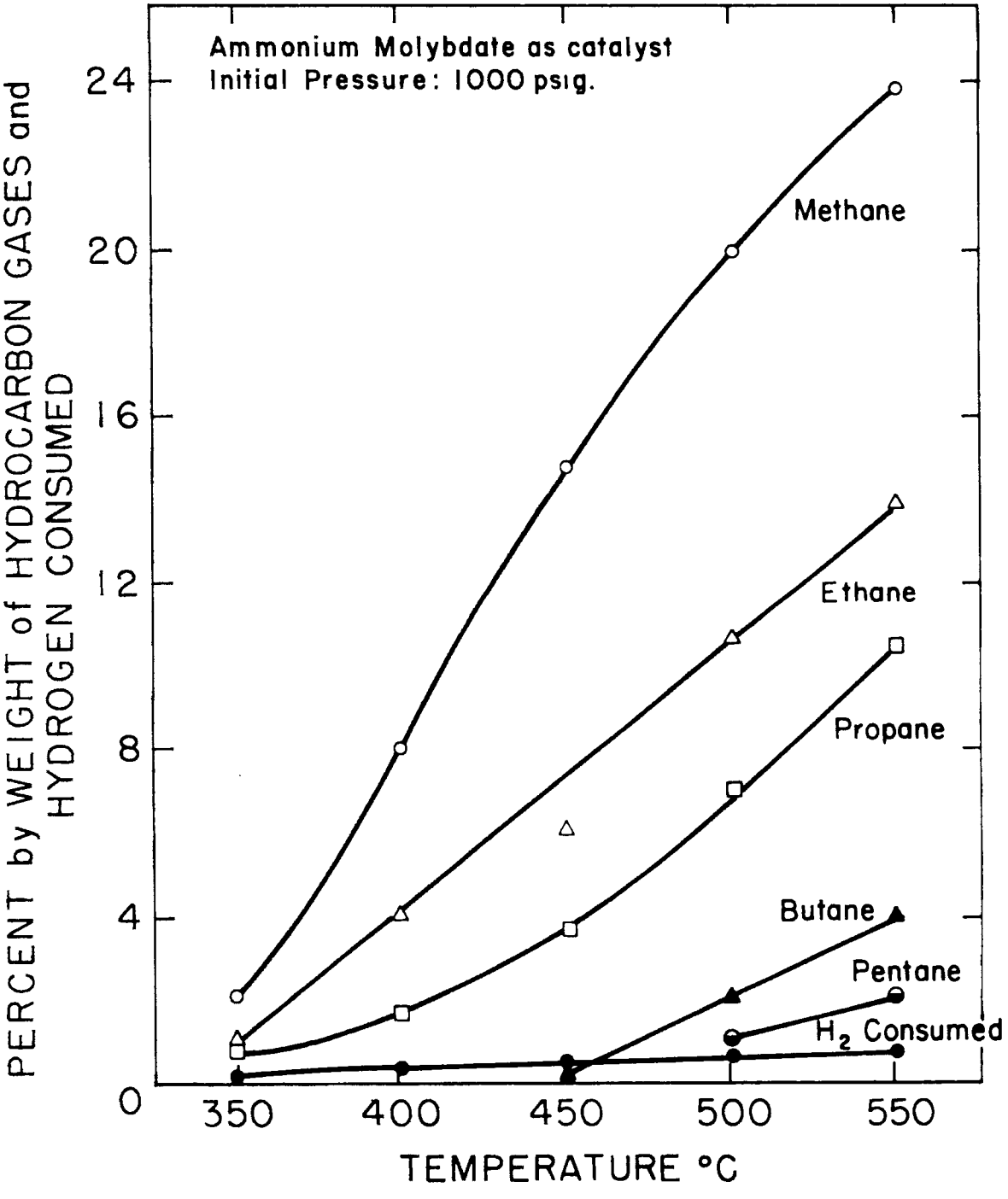

Figure 4. Effect of temperature on hydrocarbon gases yield and hydrogen consumption during batch hydrogenation of Spring Canyon coal of Utah.

The effect of hydrogen pressure upon yield of the various products is shown in Figure 5. The effect of particle size upon product yield is shown in Figure 6.

A typical representation of product distribution as a function of time is given for 450°C in Figure 7. In general the yield of liquids reached a maximum for a given temperature, then decreased at longer times with a concurrent increase in gaseous yield, due to cracking reactions.

The hydrogen consumption as a function of time is shown in Figure 8 for the various temperatures. It is noted that at the higher temperatures hydrogen is produced faster than it is consumed as time increases, resulting in a net gain in hydrogen in the system.

Table I gives the percent by volume of acids, bases and neutral oil in the liquid product. Table II gives the percent by volume of aromatics, olefins and saturates in the neutral oil fraction.

When the optimum conditions were applied to the several bituminous coals, the higher the volatile matter content of the coal, and the lower the fixed carbon content, the higher the conversion. Hence the order of conversion was as follows: North Thompson Creek > Rock Springs > Spring Canyon > Wellington > Coal Basin > Gerland.

References

1. M. E. El-Feky, W. H. Wiser, G. R. Hill, "Batch Hydrogenation of High Volatile Bituminous Coal," Technical Report, Department of Interior, Office of Coal Research, Contract Number 14-01-0001-271, June (1968).

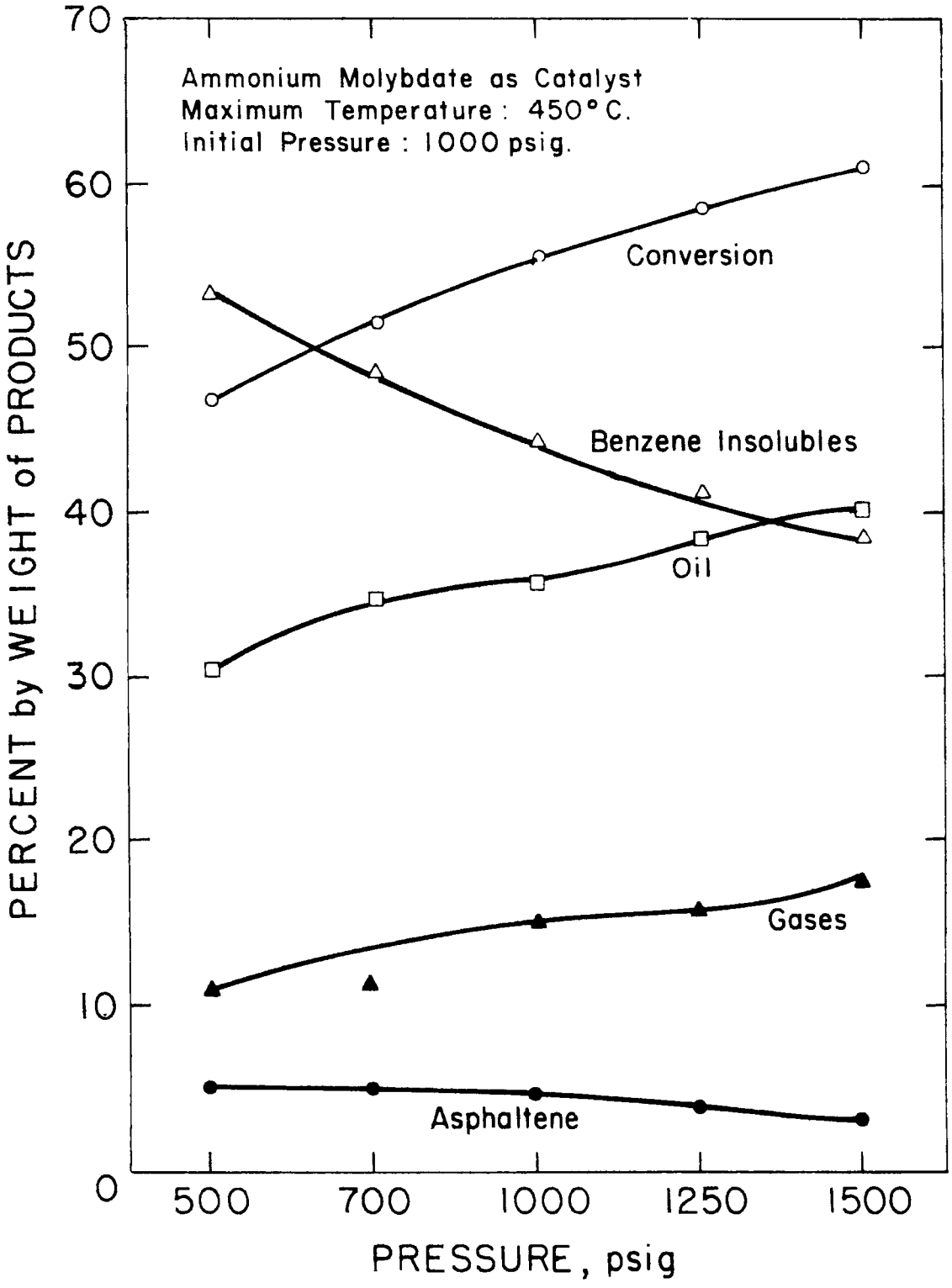

Figure 5. Effect of pressure on batch hydrogenation of Spring Canyon coal of Utah.

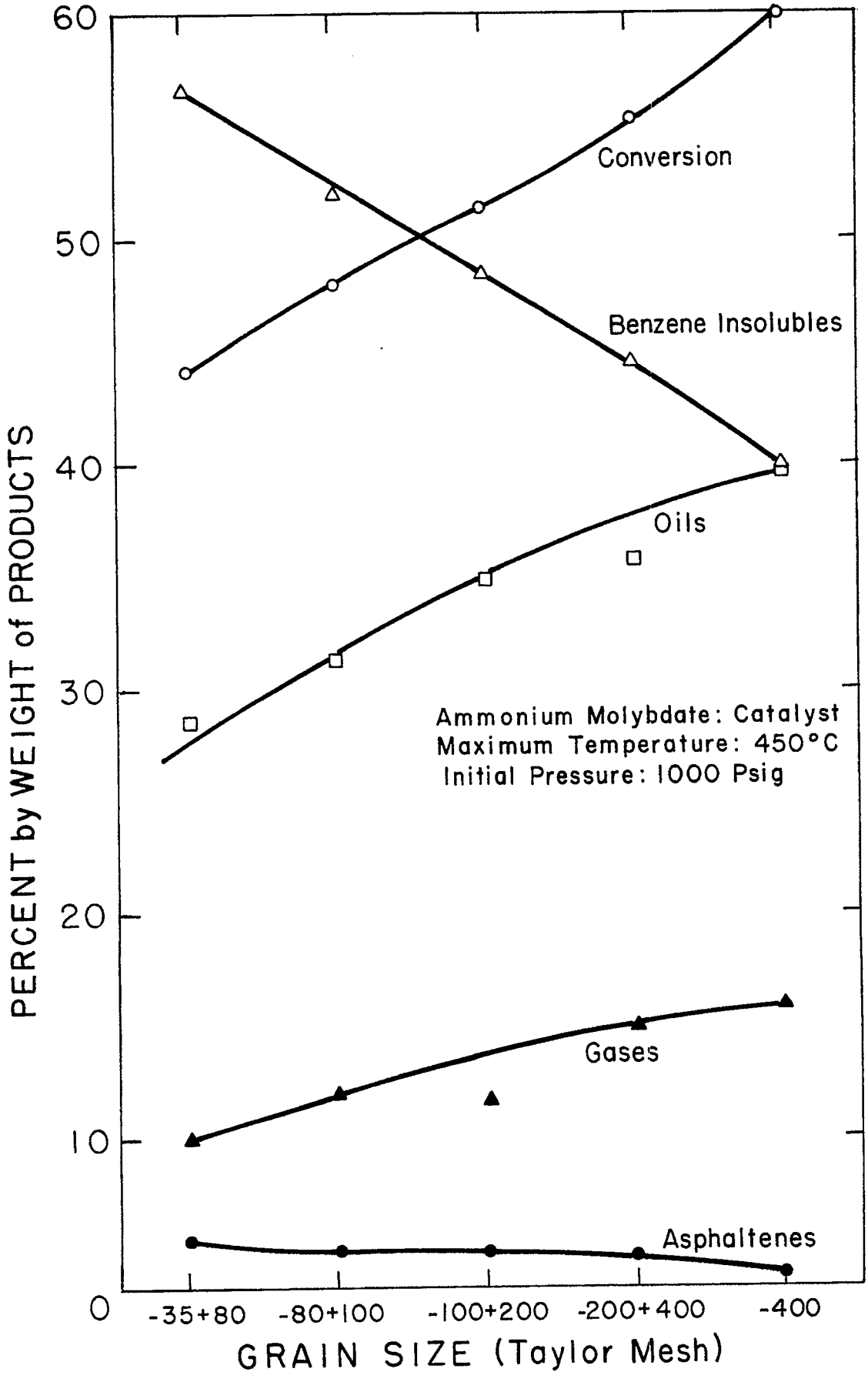

Figure 6. Effect of grain size of coal on batch hydrogenation of Spring Canyon coal of Utah.

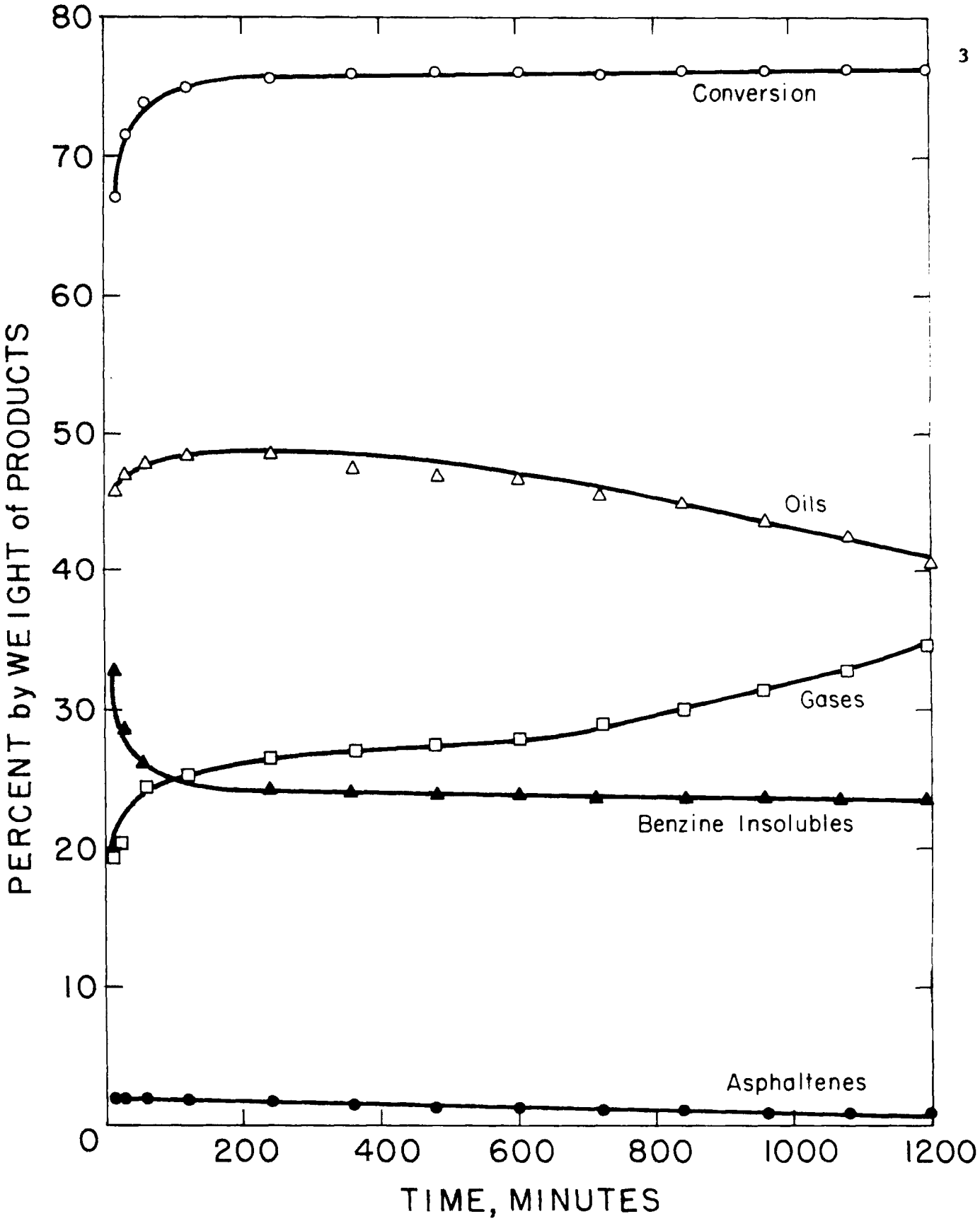

Figure 7. Products distribution of batch hydrogenation of Spring Canyon coal of Utah at 450°C.

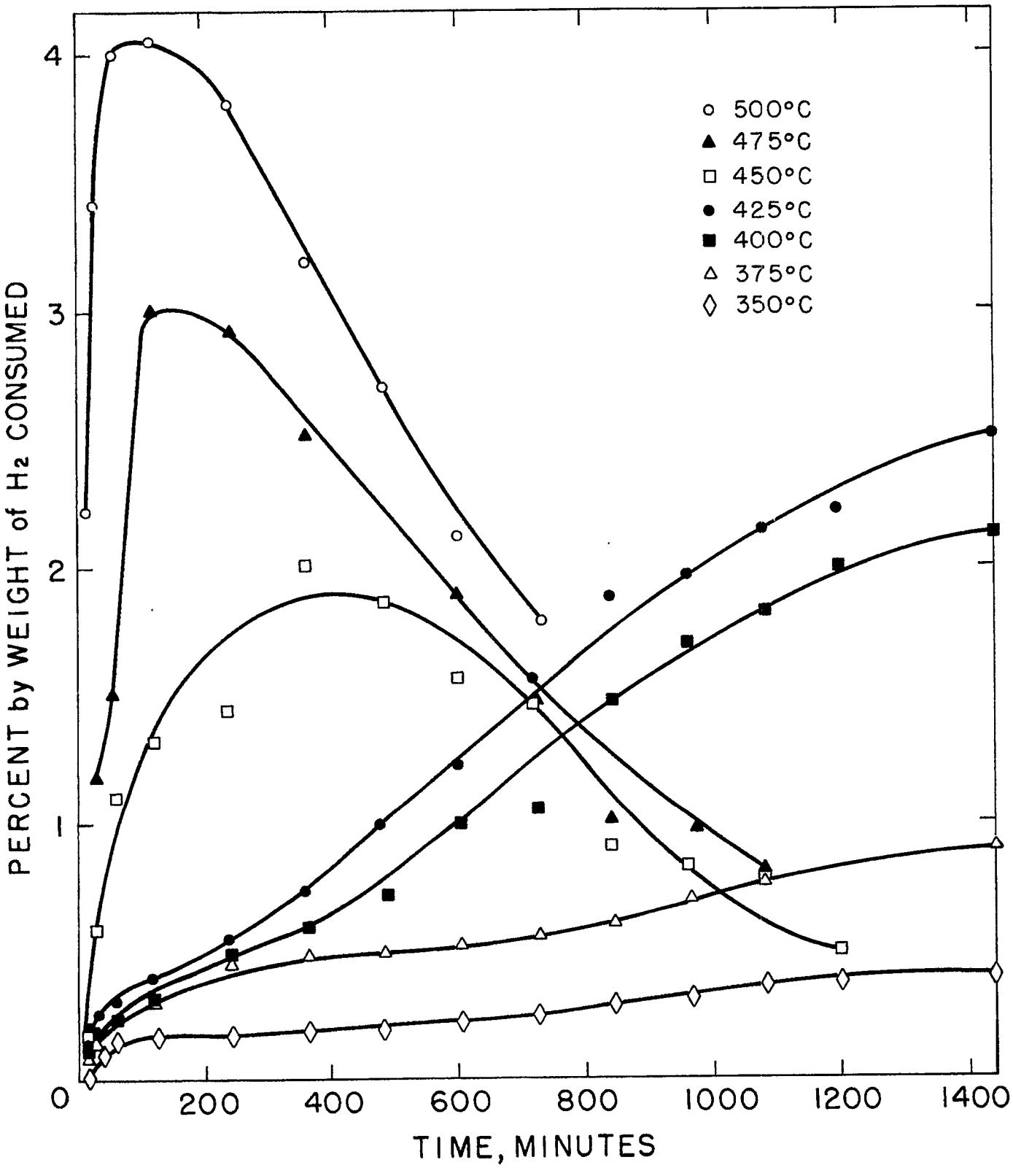

Figure 8. Percent by weight of hydrogen consumption vs. time-curves of batch hydrogenation of Spring Canyon coal of Utah.

TABLE I

% BY VOLUME OF ACIDS, BASES AND NEUTRAL COMPONENTS OF OILS

Temperature % By Wt. Time (minutes)	350°C			375°C			400°C			425°C		
	acid	base	neutral	acid	base	neutral	acid	base	neutral	acid	base	neutral
15	27.24	20.69	62.07	27.27	18.18	54.55	20 87	9.79	69.34	15.77	7.87	76.36
30	24.71	16.12	59.17	23.08	15.38	52.37	20.51	9.72	69.77	17.19	8.23	74.58
60	23.04	17.39	59.57	26.58	14.12	59.40	19.19	10.12	70.69	17.20	8.30	74.50
120	21.32	15.26	64.62	24.83	15.19	59.98	21.44	8.14	70.42	16.69	9.12	74.19
240	22.11	18.49	59.40	25.48	17.23	57.29	22.59	9.53	67.88	15.50	8.50	76.00
360	20.59	14.71	64.70	22.51	13.88	63.61	23.00	9.49	67.51	13.81	8.50	77.67
480	19.82	16.11	64.07	20.00	10.72	69.38	21.45	8.91	69.64	14.77	7.91	77.32
600	24.18	11.11	64.71	20.22	11.35	68.43	20.25	8.99	70.76	14.75	7.00	78.25
720	23.64	13.56	62.80	18.43	9.62	71.95	18.71	8.54	72.75	12.51	6.49	81.00
840	17.88	14.32	67.80	17.50	6.19	76.31	16.12	6.53	77.35	12.31	6.50	81.19
960	17.76	11.32	70.92	17.41	7.23	75.36	13.71	6.29	80.00	10.78	6.00	83.22
1080	19.33	10.91	70.36	16.12	8.13	75.75	12.84	7.11	80.05	8.91	5.12	85.97
1200	16.67	8.83	74.50	15.00	5.59	79.41	10.81	5.00	84.19	8.88	3.59	87.53
1440	15.00	8.06	76.94	15.00	6.70	78.29	9.34	5.14	85.52	7.59	3.69	88.72

TABLE I (Continued)

450°C			475°C			500°C		
acid	base	neutral	acid	base	neutral	acid	base	neutral
19.31	7.59	73.10	20.19	9.22	70.59	9.30	7.00	83.70
16.17	5.61	78.22	17.29	7.31	75.40	8.00	7.21	84.79
17.52	5.96	76.52	14.52	5.88	79.60	6.20	6.00	85.80
17.00	6.00	77.00	11.98	3.77	84.25	9.50	6.09	85.36
16.87	5.45	77.68	11.00	4.00	85.00	7.50	6.61	85.89
16.51	5.00	83.49	12.10	3.98	83.92	8.71	6.44	84.85
15.50	4.28	80.22	5.62	2.25	92.13	6.00	5.50	88.50
14.00	4.15	81.85	8.00	6.00	86.00	5.20	5.80	89.00
11.22	3.00	85.78	8.88	2.98	88.14	4.18	2.99	92.83
12.29	3.50	84.21	10.00	3.10	86.90			
9.55	3.34	87.13	7.28	2.90	90.32			
10.97	3.00	86.03	6.00	2.90	91.10			
7.16	2.99	89.85						

TABLE II

% BY VOLUME OF AROMATICS, OLEFINS AND SATURATES IN THE NEUTRAL OILS

Temperature	350°C			375°C			400°C			425°C		
% by wt. time (minutes)	aro-matics	olefins	satur-ates	aro-matics	olefins	satur-ates	aro-matics	olefins	satur-ates	aro-matics	olefins	satur-ates
15	74.88	25.12	10.00	60.80	19.20	20.00	59.73	16.13	24.14	54.95	18.31	26.74
30	64.89	25.00	10.11	61.78	22.60	15.62	58.75	17.25	24.00	56.14	17.98	25.88
60	64.37	25.55	9.08	60.84	25.88	13.28	59.66	16.00	24.34	54.59	17.00	28.41
120	64.78	24.00	11.22	55.18	25.00	19.82	60.02	15.98	24.00	56.44	19.20	24.36
240	74.65	25.20	8.15	54.30	26.70	19.00	59.50	16.00	24.50	55.45	16.55	28.00
360	67.00	24.00	9.00	62.01	21.20	16.79	58.80	15.00	26.20	52.62	15.80	31.58
480	61.76	23.00	15.24	63.73	19.00	17.27	59.26	10.31	30.43	58.18	10.00	31.82
600	64.86	22.80	12.34	61.69	18.98	19.33	62.01	9.99	28.00	61.48	8.99	30.53
720	65.50	22.50	12.00	63.48	18.90	17.62	75.00	9.00	26.00	49.20	9.50	41.30
840	68.53	21.98	10.55	59.23	18.97	21.20	54.40	10.50	35.90	58.32	6.00	35.68
960	67.12	21.00	11.88	60.18	18.02	21.82	58.35	3.45	38.20	50.32	8.68	41.00
1080	68.00	20.00	12.00	58.94	19.31	21.75	58.08	7.00	34.92	52.75	8.00	42.25
1200	66.89	20.11	13.00	60.50	17.50	22.00	52.23	3.33	44.44	46.90	6.81	46.29
1440	64.00	21.50	13.50	62.73	15.28	21.99	49.33	3.17	47.50	47.08	4.38	48.54

TABLE II (Continued)

450°C			475°C			500°C		
aro-matics	olefins	satur-ates	aro-matics	olefins	satur-ates	aro-matics	olefins	satur-ates
59.02	10.98	30.50	61.56	8.11	30.33	58.60	9.00	32.40
59.78	8.00	33.22	69.25	6.15	35.00	53.38	6.50	40.12
59.41	12.04	28.55	55.10	6.00	38.90	51.49	4.22	44.29
60.42	11.58	28.00	50.12	7.88	42.00	55.06	2.39	42.55
57.41	8.51	34.08	52.00	6.50	41.50	51.10	2.00	46.90
59.77	7.00	33.23	51.34	7.01	41.65	54.79	2.50	43.41
57.56	7.00	35.44	51.50	6.00	42.50	44.80	3.32	51.88
55.71	6.29	38.00	44.61	5.89	49.50	46.60	3.40	50.00
56.11	5.89	38.00	50.11	5.89	44.00	48.63	2.98	48.39
55.54	5.33	40.13	49.80	5.00	45.20			
50.26	4.50	45.24	46.39	4.09	49.54			
52.11	4.00	43.89	43.82	3.90	52.28			
50.29	4.21	45.50						

Projects III(d) and X. REACTIONS OF COAL LIQUIDS

Liquid and gaseous materials are derived from coal when it is subjected to a variety of procedures. Pyrolysis, hydrogenation and dissolution in solvents are examples of these techniques. The gaseous materials are generally simple mixtures of a few hydrocarbons and common inorganic gases. These samples lend themselves to rapid and accurate analysis by means of conventional gas chromatography. This is not true for the liquid products derived. The liquids are complex mixtures of many different organic materials, including aliphatic, olefinic, aromatic, heterocyclic and polar compounds. The complexity is such that no single analytical technique is adequate for characterization.

Some sort of separation procedure is required to reduce the complexity of liquid samples and make the fractions amenable to analysis. Distillation has been used for this separation and is useful for the lower boiling fractions because these can be characterized by gas chromatography. However, the higher boiling fractions are still much too complicated. Also, problems connected with cracking at high distillation temperatures, and rapid polymerization of the products makes distillation an undesirable separation procedure. Further, the upper temperature limit of the gas chromatographic method places a ceiling on the distillation fractions that can be characterized in this manner.

Because of the many limitations of the distillation-gas chromatographic procedures it was found expedient to seed alternate methods for the separation and characterization of coal liquids. A low temperature separation would be the first step in such a procedure. The most successful approach to this separation has been that of Gel Permeation Chromatography (GPC). This method permits a separation based on molecular size. If a proper column support material is used, it is possible to make some separation based on the chemical polarity or reactivity of the components. The major work of this nature done under the contract was published as an OCR Technical Report in May of 1969 entitled "Fractionation of Low Temperature Coal Tar by Gel Permeation Chromatography," by Hsieh, Wood, Anderson and Hill. This information was presented as a technical paper with the same name at the 157th National Meeting of the American Chemical Society in April, 1969.

The physical separation of complicated mixtures based on GPC is fundamentally one of molecular weight or molecular size. The column support is composed of polymer beads. The beads are highly porous in nature but the cross linking of the polymer chains has been controlled to produce pores of nearly the same size. If the pores are of such a size that some molecules can diffuse into the pores but others are excluded because of their size, a difference in path length for the two species will result. The smaller molecules can diffuse into the pores and therefore travel a longer path in going the length of the column than do the large molecules. The ultimate result is that the large molecules pass through first and the small molecules come through later.

The major portion of the GPC work done at present is performed with non-polar polystyrene gels with controlled pole sizes. These gels separate on molecular size only and hence provide a measure of molecular weight. Actually the result is a molecular weight distribution. However, some gels are polar in nature, that is they contain chemically reactive groups that can act in an ion exchange capacity. Such a gel is Sephadex LH-20 used in the work on coal tars. This gel is a polymerized dextran and it contains many hydroxyl groups capable of exchanging with charged or polar molecules passing through. Because of its immunity to attack by organic solvents, it is suitable for use with solvents such as tetrahydrofuran (THF), benzene, toluene, or alcohols. For our work THF was chosen as a solvent because it was better able to dissolve the higher molecular weight components in coal tar. Sephadex LH-20 with THF as a solvent acts to separate coal tar materials by both molecular weight and chemical reactivity. The result is a spectrum of materials, first of aliphatic hydrocarbons, from high to low molecular weight, then aromatic hydrocarbons from high to low molecular weight followed by tar acids and bases from high to low molecular weight.

The separation effect on pure materials of various types is indicated in Figure 1. Aliphatic and aromatic materials were used in producing the data for this figure. The differentiation between aliphatic and aromatic materials in coal tar occurs near fraction number 65 or an elution volume of 225 milliliters. This statement must be limited to the case where light hydrocarbons, expecially aliphatic, have been removed by distillation. If the light hydrocarbons (C_6 to C_{12}) are included, we can expect an overlap of the aliphatic and aromatic peaks. Figure 2 shows a typical GPC chart for a low temperature coal tar, in this case the 150 to 350°C fraction from Spring Canyon Coal tar. If the material boiling below 150°C is not removed the valleys between the peaks would be less pronounced. The first peak represents aliphatic, the second peak represents aromatic and the third peak represents tar acid and base materials.

The verification of the materials to be found in each area of the GPC chart was made by gas chromatographic analysis of individual fraction components. This was done with two different gas chromatographic column packings and with known materials added. Chemical separation was also done by NaOH to remove the acids and H_2SO_4 to remove the bases from the original coal tar. A pyridine extraction was used to remove aromatic and tar acid components from the aliphatic materials.

Figure 3 shows the GPC pattern for the 150 to 350°C portion of Spring Canyon coal tar with the same for the 350 to 550°C portion. The higher boiling portion contains higher molecular weight components in both the aliphatic and aromatic areas of the chromatogram. Less tar acid and base components are present in the higher boiling fraction.

Figure 4 shows a comparison of four different coal tars by GPC. These are the 150 to 550°C tars from Spring Canyon, Utah, Big Horn, Wyoming, and River King, Illinois. The fourth tar was produced by the FMC process from Hiawatha, Utah coal. Tar sand extracts, shale oil distillates and a crude petroleum from the Red Wash, Utah oil field are shown in Figure 5.

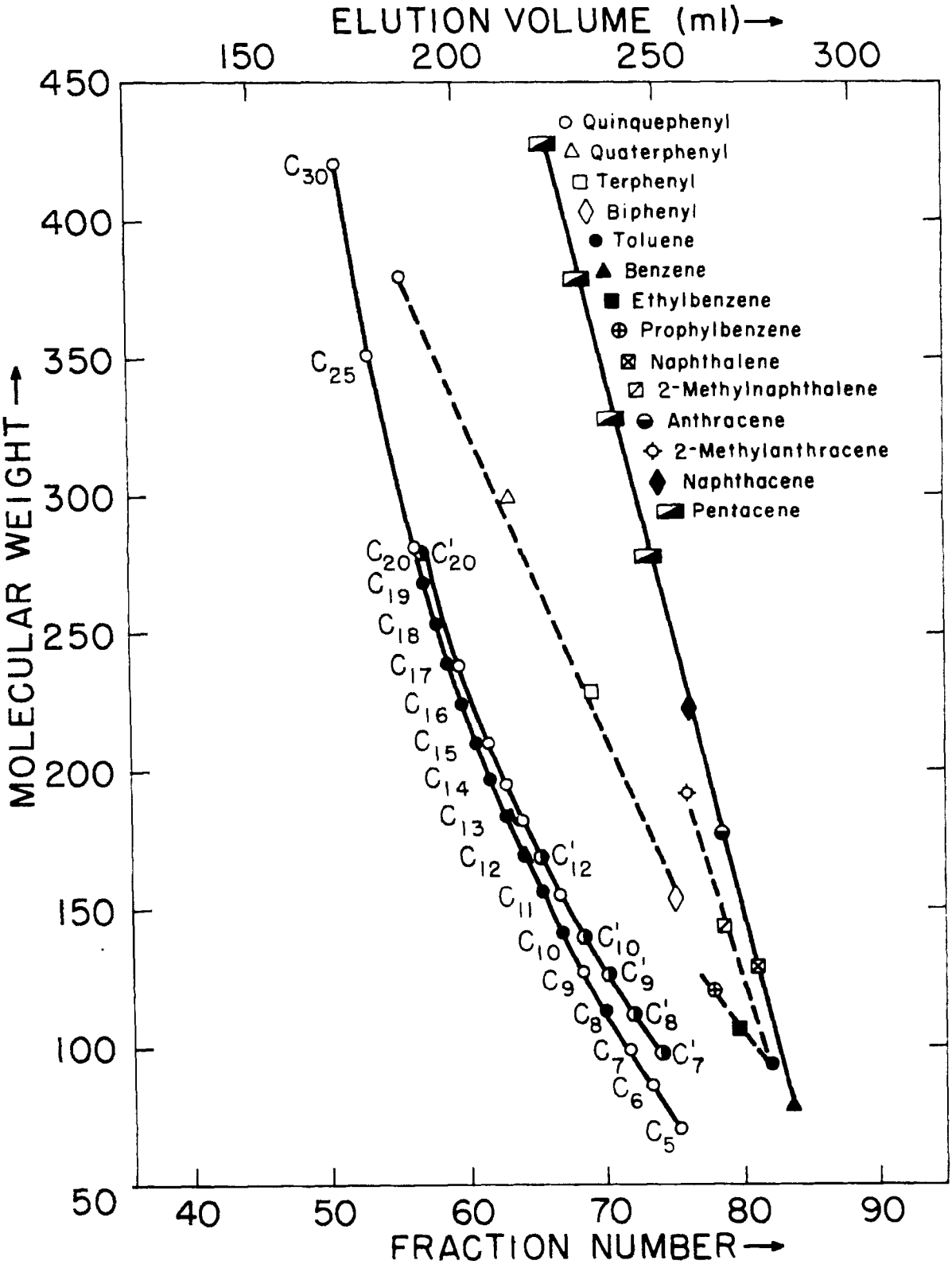

Figure 1. GP Chromatography of known hydrocarbons: paraffins, olefins, and aromatics.

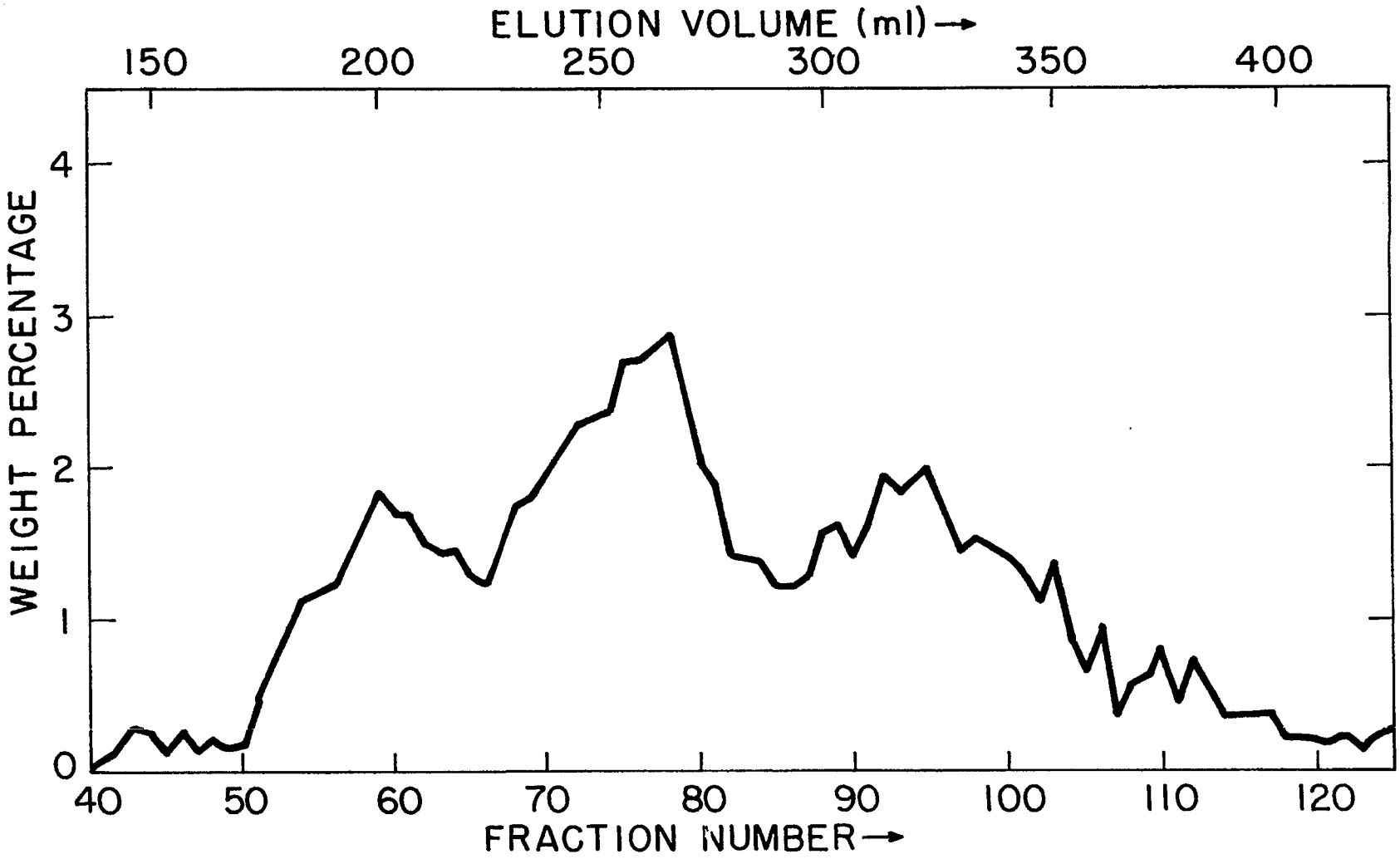

Figure 2. Elution curves (GPC) of low temperature coal tar distillates (150°-350°C) from Spring Canyon coal.

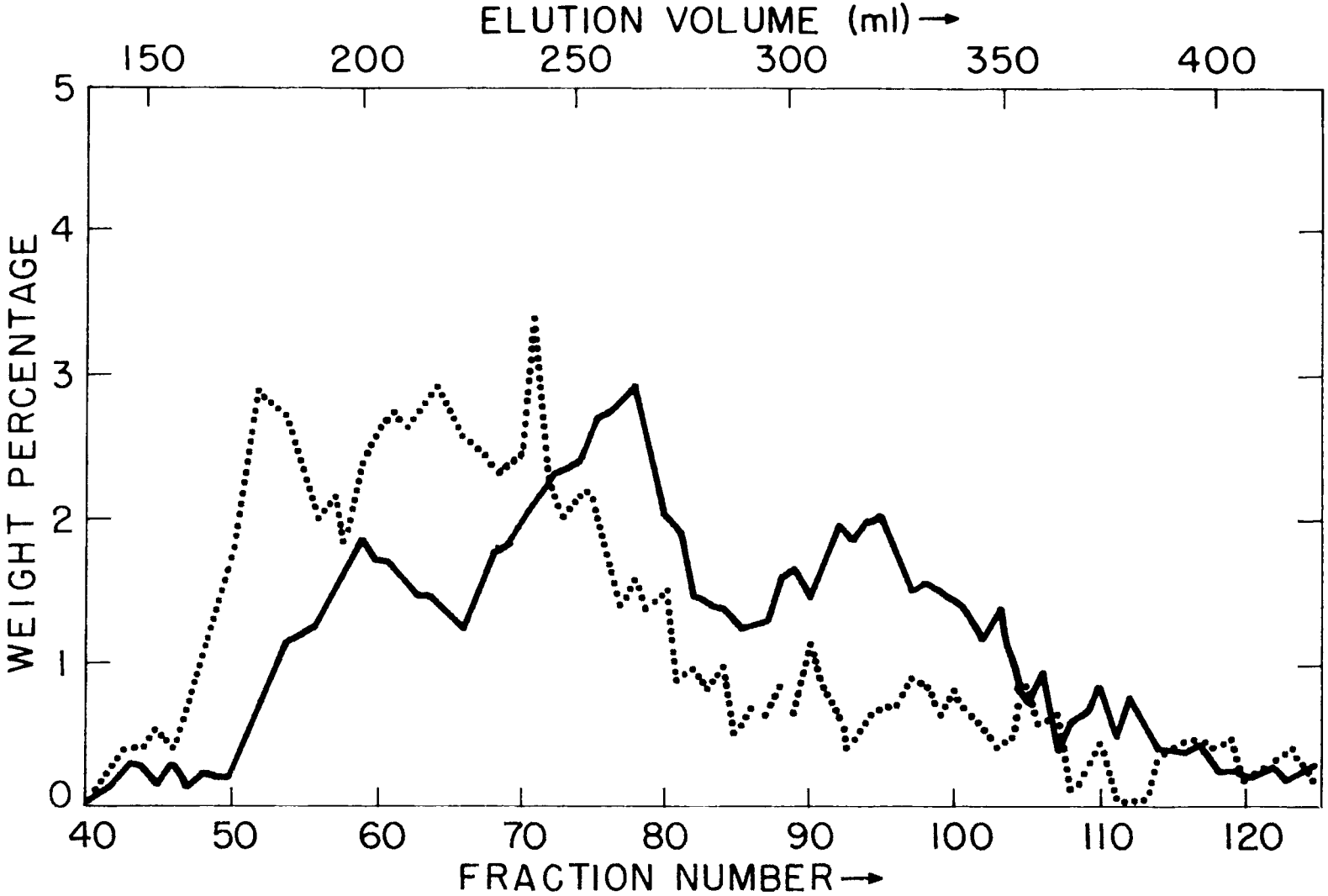

Figure 3. Elution curves (GPC) of distillates (150°-350°C) and pitch (350°-550°C) from Spring Canyon coal tar.

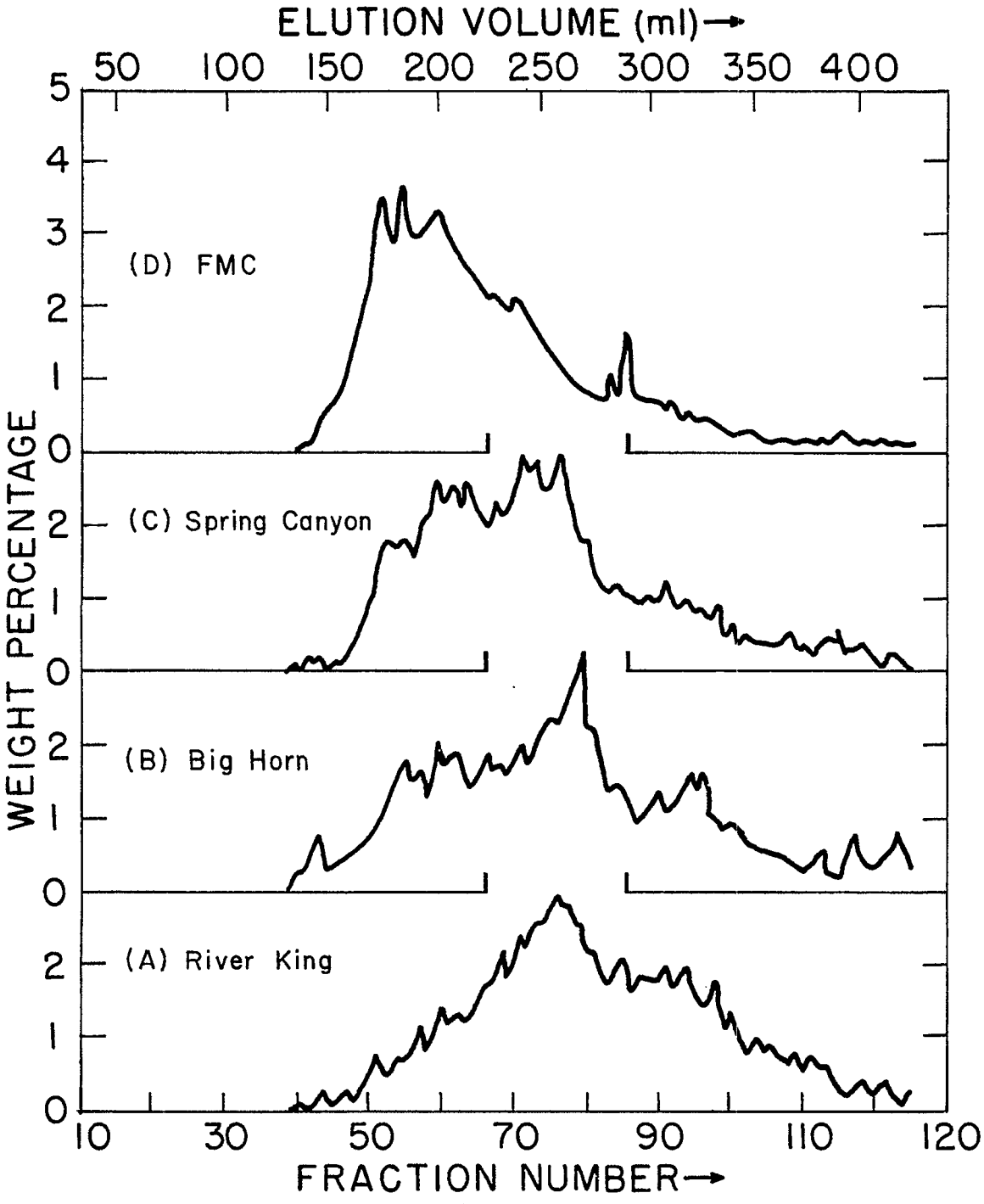

Figure 4. GPC elution curves.

(A) River King coal tar (150°-550°C).
(B) Big Horn coal tar (150°- 550°C).
(C) Spring Canyon coal tar (150°-550°C).
(D) FMC Pyrolysis Coal Tar.

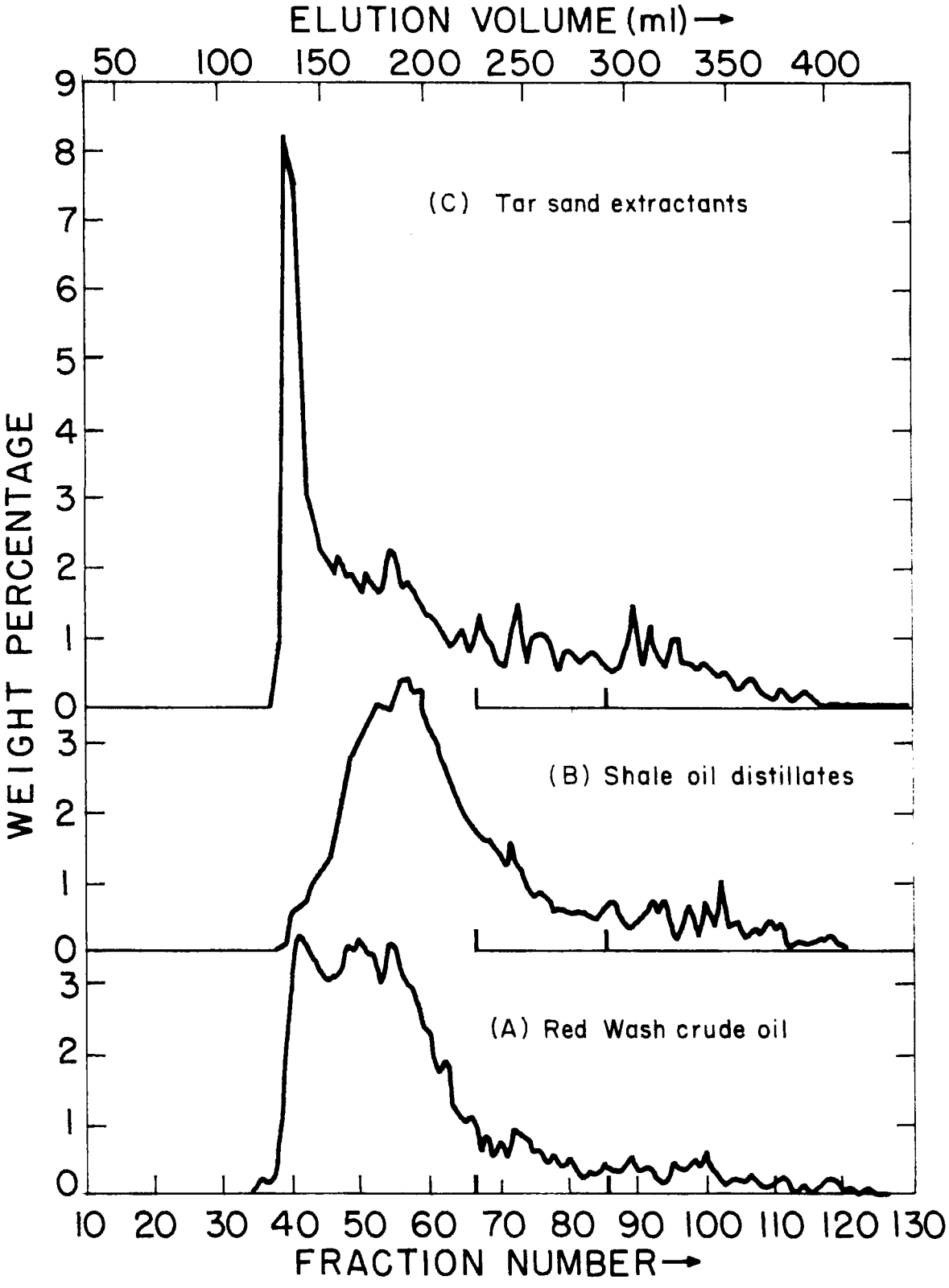

Figure 5. GPC elution curves.

A comparison of the results calculated from these chromatograms is shown in Table I. In these calculations, the aliphatic and aromatic composition is more accurate than the tar acids due to uncertainty as to the level of the background after the sample has passed through the column.

Efforts to apply the method of GPC to coal hydrogenation liquids have demonstrated a greater uncertainty in the results than occurred with coal tar. The data for coal tar was obtained by volitilizing the solvent from each fraction and weighing the residue. This procedure is very time consuming and may introduce errors. Therefore, a commercial GPC unit has now been obtained. Determinations are made with a differential refractometer that is considerably more reliable than the weight-of-residue technique. The unit is in the installation stage and will be standardized and applied to coal hydrogenation liquids.

The quality of reproduction using the fraction residue weight method is shown by the data of Table II. One further factor which must be investigated with respect to this uncertainty is the change of composition due to polymerization or oxidation over a period of time. The weight-of-residue procedure requires approximately three days to complete one sample while the new unit will make the separation, on a much smaller sample, in a few hours. The long delay with the weight-of-residue method makes it possible that polymerization, oxidation and similar reactions could have contributed to the composition changes.

TABLE I

PERCENTAGE RESULTS FROM GPC FRACTIONATION METHOD

	I aliphatics 30-60	II aromatics 67-85	III tar acids 86-125
Red Wash (Crude oil)	82.21% (87.89%)*	11.33% (12.11%)*	6.46%
Tar sand (Benzene extractants)	69.10% (79.30%)	18.04% (20.70%)	12.86%
Shale oil (Distillate from Rifle, Colorado)	68.24% (83.21%)	17.77% (16.79%)	13.99%
F.M.C. (Pyrolysis coal tar)	57.71% (67.89%)	27.30% (32.11%)	14.99%
Spring Canyon (High volatile bituminous coal)	37.22% (47.98%)	40.36% (52.02%)	22.42%
Big Horn (Subbituminous coal, 17.2% O_2)	31.21% (44.80%)	38.45% (55.20%)	30.34%
River King (High volatile bituminous coal, 3.30% S)	18.37% (29.71%)	43.47% (70.29%)	38.16%
Pitch (From Spring Canyon coal tar)	47.07% (58.87%)	32.88% (41.13%)	20.05%
Neutral oil (From Spring Canyon coal tar distillate)	41.77%	58.23%	
Tar acids from Spring Canyon coal tar by chemical method			34.36%
Neutral oil from Spring Canyon coal tar by FIA method	(38-42%)	(58-62%)	
Distillates (1) from Spring Canyon coal tar (150°-350°C)	24.09% (38.23%)	38.03% (60.43%)	37.88%
Distillates (2) from Spring Canyon coal tar (150°-350°)	22.62% (36.72%)	38.98% (63.27%)	38.40%

*The percentages of aliphatics and aromatics in the neutral oil where tar acids and tar bases have been removed are indicated by the use of parentheses.

TABLE II

REPLICATION OF GPC DATA FOR COAL HYDROGENATION LIQUIDS

Test	% Aliphatic	% Aromatic	% Tar Acid
1	13.1	64.3	22.6
2	10.7	66.9	22.5
3	12.0	67.0	21.0

Coal Hydrogenation Test # 162

Coalville Coal

-40 mesh

$ZnCl_2$ Catalyst

5 g/min Feed Rate

288 g charge

PRODUCTS

20.9% Solids

49.2% Liquids

29.9% Gases

79.1% Conversion

Project IV(a). CONTINUOUS HYDROGENATION OF COAL

A dilute phase, free-fall, solid-gaseous continuous coal hydrogenation reactor was assembled and operated under this contract. It is depicted in the schematic drawing of Figure 1. This unit was designed to permit a high degree of flexibility in operating parameters in order that the free-fall process could be investigated under widely differing conditions. With this device it is possible to drop powdered coal through a heated and pressurized reaction zone in the presence of hydrogen or other gases. The unit is capable of pressures to 5000 p.s.i., temperatures to 700°C and feed rates of 5 to 50 grams per minute. The feed hopper is capable of feeding up to five pounds of coal but the receiver for the liquids and reacted solids is limited to about two pounds. Coal powdered to less than 10 mesh can be handled by the feeding system. The remote control panel, which provides information and control capability for all aspects of the hydrogenation process is shown in Figure 2.

With this apparatus, hydrogenation data has been gathered on a number of Western United States coals and some other coals for comparison purposes. The most extensive study was made with coal from the Spring Canyon Mine in Carbon County, Utah. This information was published as a technical report (Haddadin, Anderson, Hill, "Dilute Phase Hydrogenation of High Volatile Bituminous Coal," June, 1968). and presented as a paper before the National Meeting of A.I.Ch.E., Los Angeles, California, December, 1968.

Some of the technical problems connected with the operation of the device were discussed in a paper entitled "Operating Variables of a Continuous Coal Hydrogenation Reactor" presented before the 1969 Northwest Regional Meeting of the American Chemical Society in June, 1969, held in Salt Lake City, Utah.

It was found early in the operation of this reactor that special care would be required in coal preparation. The coal feed must be completely dry and devoid of any sticky components or the charge will not feed from the hopper (Vessel B, Figure 1). Several approaches have been tried in an effort to overcome this difficulty. The work on Spring Canyon Coal was done by the addition of coke breeze in a 1:1 ratio. This does make it possible to feed the charge. Actually the amount of coke to be added is dependent on the particle size of the coal. With -10 or -20 mesh coal no coke is required, but with -200 mesh coal a ratio of 1:2 coal to coke is required. For the majority of the Spring Canyon Coal study a 40-80 mesh particle size and a 1:1 ratio of coal to coke were used.

A second operational problem with the reactor has been the fact that coal particles passing through the hot zone will stick to the hot walls, become devolatilized and build up a coke layer. Depending on the rate of build up, the operation of the reactor may be curtailed rapidly by bridging of the hot zone.

The nature of the Spring Canyon Coal study was such that samples small enough to avoid bridging within the reactor were used. The product of each test then resulted from some hydrogenation and some pyrolysis of the coal.

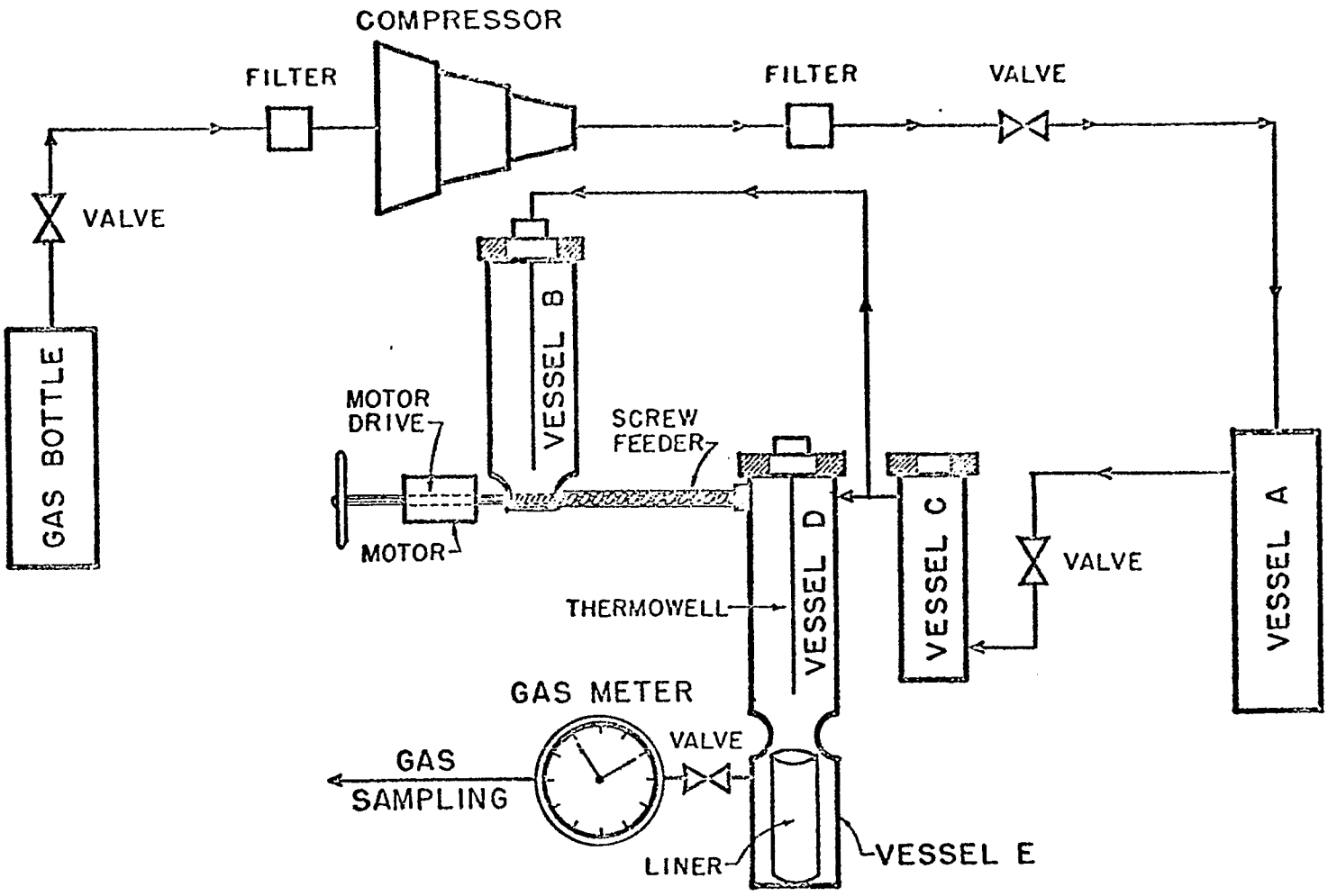

FIGURE I. EQUIPMENT-SCHEMATIC DIAGRAM

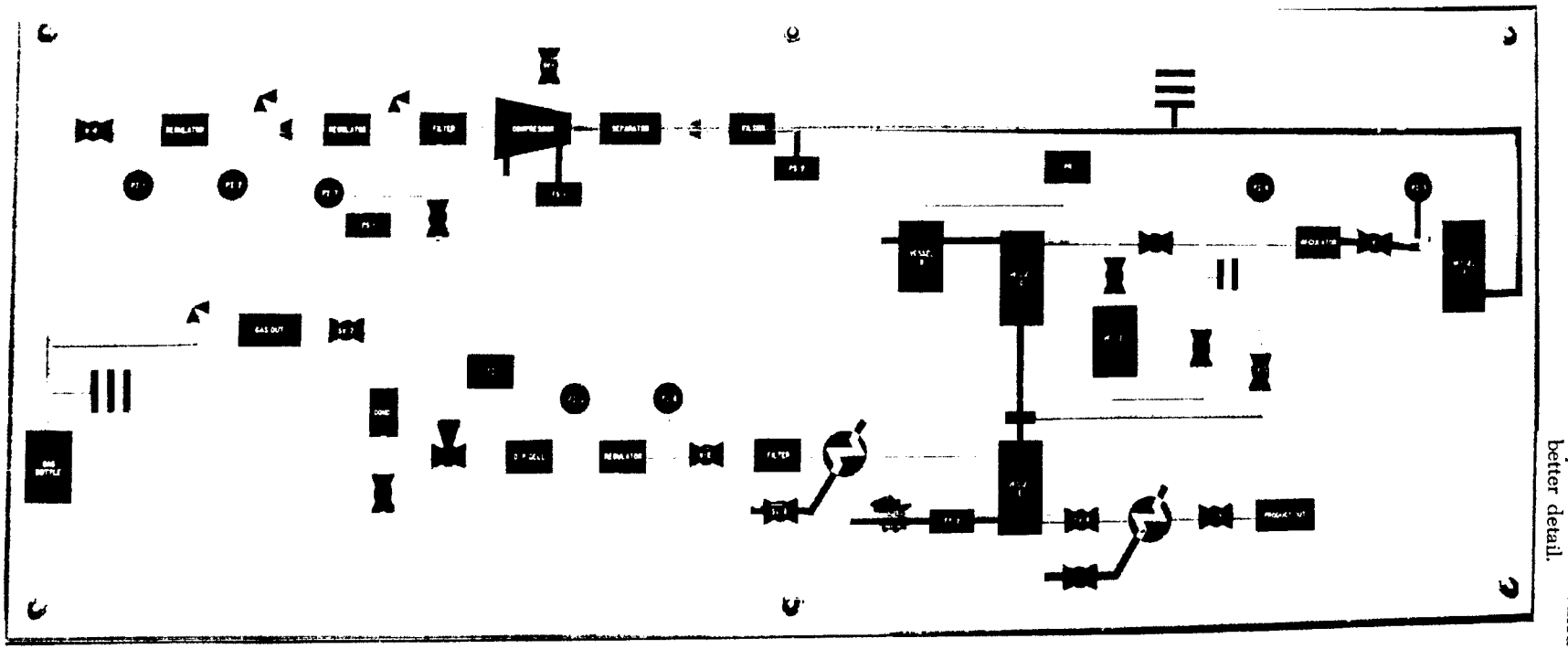

Figure 2. Flow diagram of OCR continuous coal hydrogenation unit.

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The selection of appropriate operating conditions for Spring Canyon coal followed a study of pressure, temperature, catalyst, catalyst concentration and particle size on coal coke mixtures using this coal. Figure 3 shows the effect of temperature on the production of liquid and solid products and the total conversion of the coal. The data is shown in Table III, Appendix A. This led to the selection of a temperature of 515-525°C as the best operating temperature, simply because this point represented a maximum in liquid production.

Figure 4 represents a study of the pressure effect on Spring Canyon coal and resulted in the selection of 2000 P.S.I. as an operating pressure. This data is presented in Table II, Appendix A. There is apparently no improvement in liquid conversion or total conversion for higher pressures.

A study of the literature[1,2,3,4,5,6] indicated that Stannous chloride is a good hydrogenation catalyst for the conversion of coal to oil and gas. Therefore, this catalyst, applied as a solution in hydrochloric acid to the coal particles and then dried for maximum penetration of pores was used for the majority of the work. Figure 5 (Table III, Appendix A) indicates that about 15 percent of stannous chloride applied to the coal yields a maximum conversion to liquid products and a maximum total coal conversion.

A study of the coal particle size, as shown in Figure 6 (Table IV, Appendix A) indicates that increased conversion is to be expected from continued reduction in particle size. The problem of sample feeding to the reactor, however, dictates the use of a large particle size. Therefore, a compromise at 40-80 mesh was selected for the majority of the work.

In this study, the degree of conversion of Spring Canyon coal was found to be independent of the feed rate. However, since the control of a uniform reactor temperature is difficult at feed rates higher than 20 grams per minute, actual tests were run at low feed rates, usually 5 grams per minute.

Variation of the hydrogen flow rate apparently has little effect on the degree of conversion. High flow rates, however, (over 30 liters per minute) dilute the product gases and make their determination difficult. Low flow rates are difficult to reproduce from one test to the next. For these reasons an optimum flow rate in the range of 12-15 liters per minute was used.

Once the optimum values of the operating variables were established for Spring Canyon coal, the same conditions were applied to a series of coals from Utah and Wyoming. The results of these trials are shown in Table V, Appendix A. Percent conversion, percent oil, percent asphaltene and percent gas are included for each coal. This table provides a comparison of the hydrogenation activity to be expected from six different coals.

The problem of feeding coal from the hopper to the reactor can be controlled in two different ways. The addition of coke of the same particle size, as previously mentioned acts to reduce the sticking tendency. Agglomeration of the fine material with 0.5 - 1.0 percent starch also makes the charge flow more smoothly. In the Spring Canyon coal study the problem

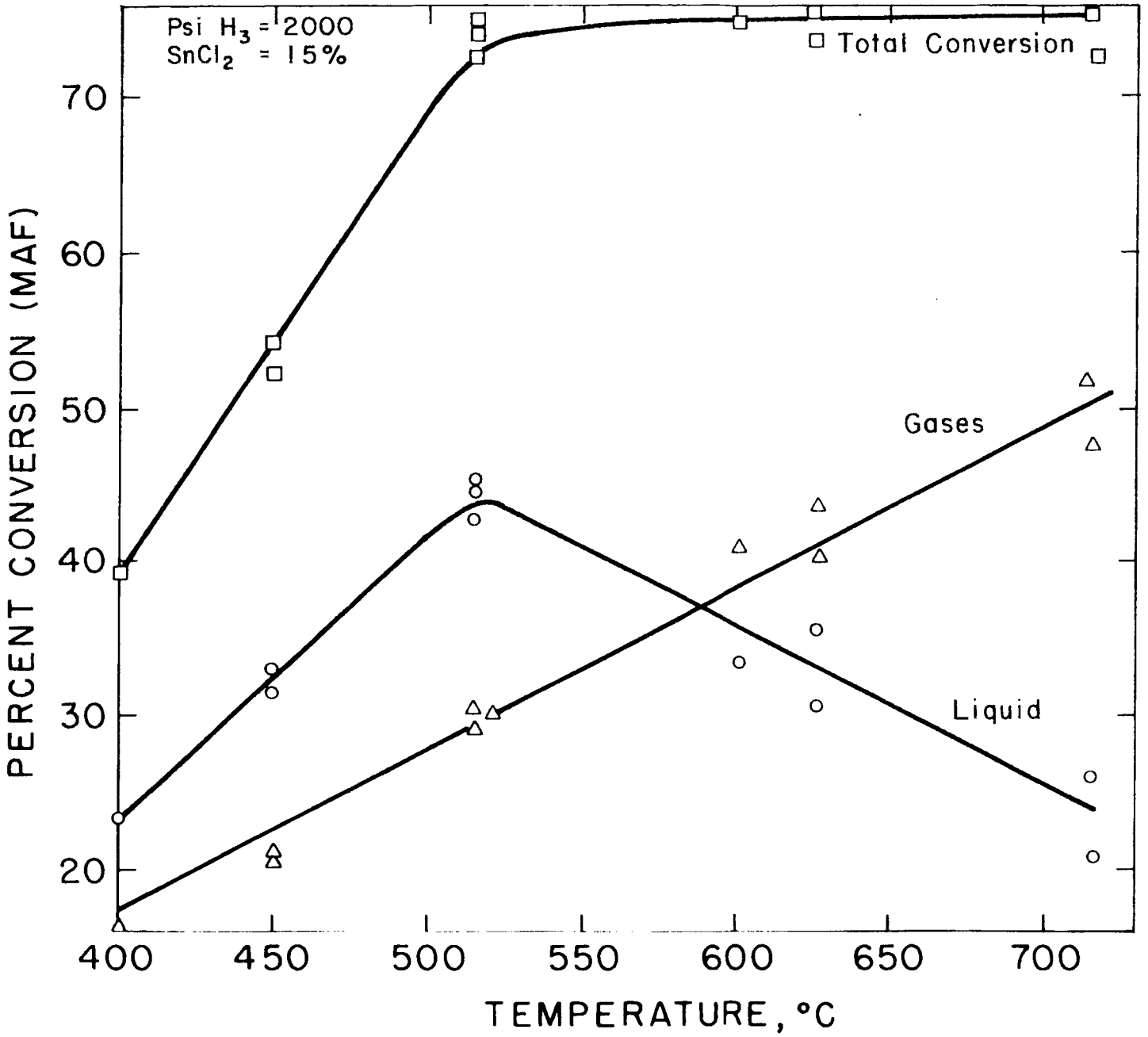


Figure 3. Spring Canyon coal (40 - 60 Mesh.)

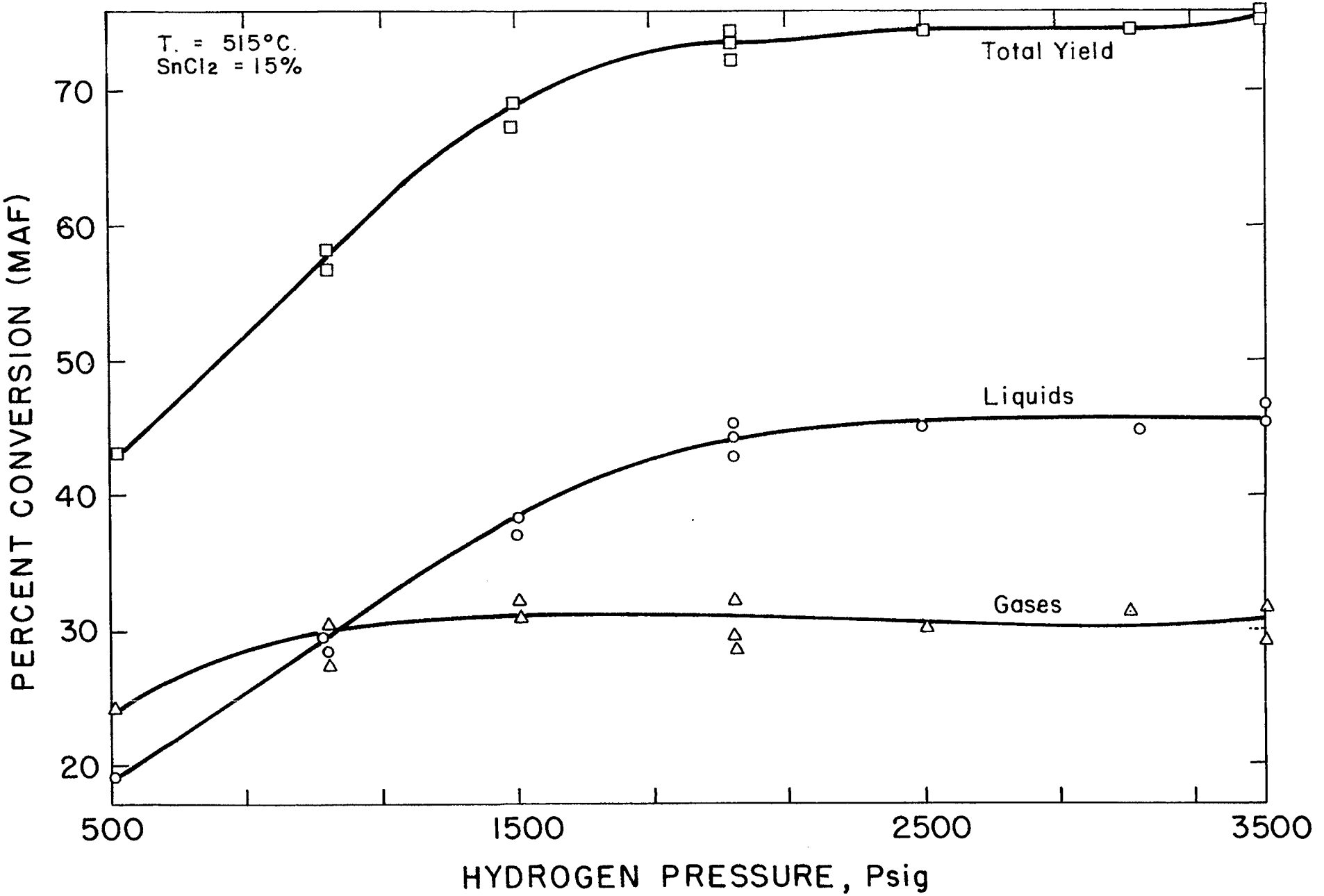


Figure 4. Spring Canyon coal (40 - 80 Mesh.)

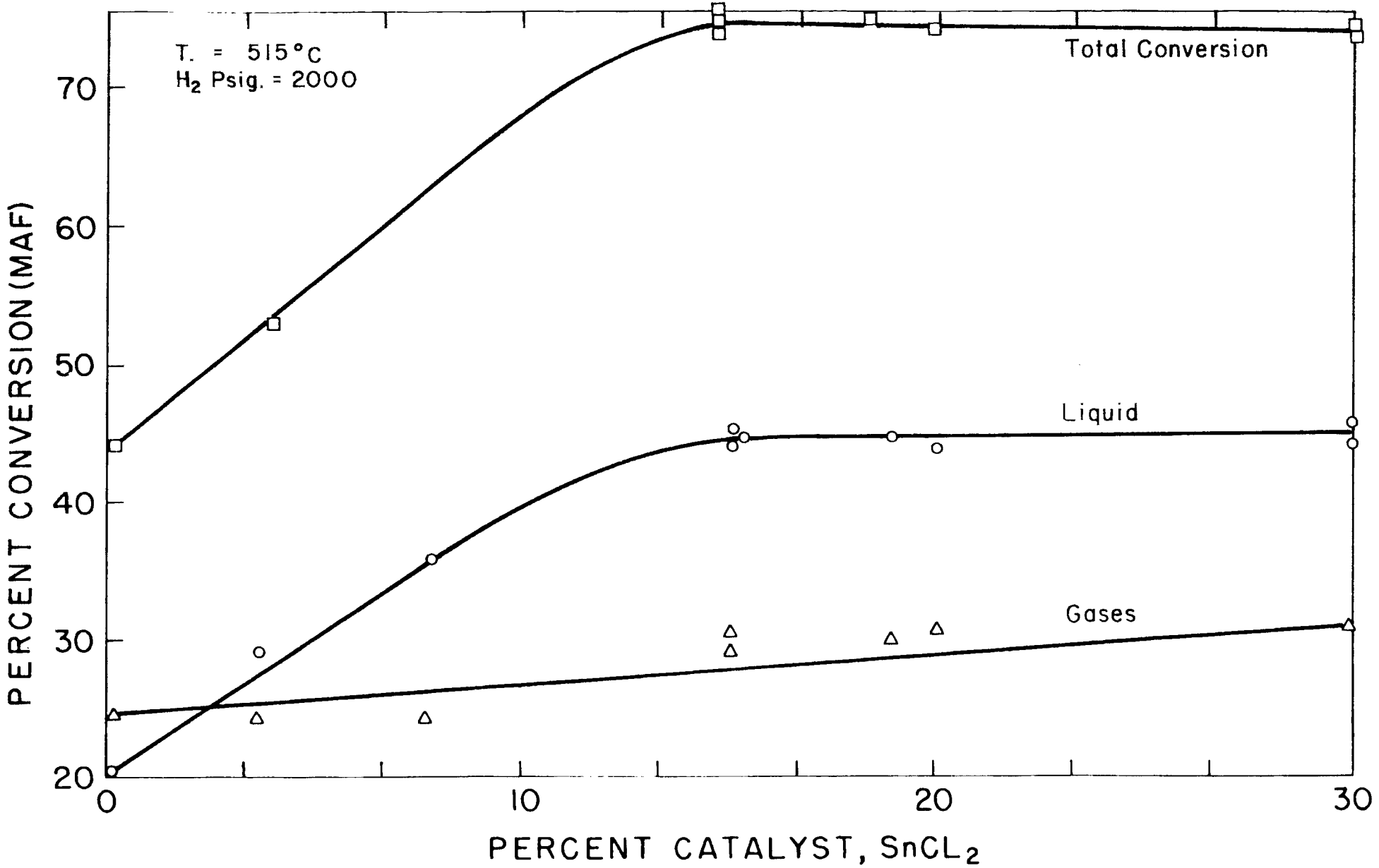


Figure 5. Percent Catalyst vs. Yield, Spring Canyon coal (40-80 Mesh)

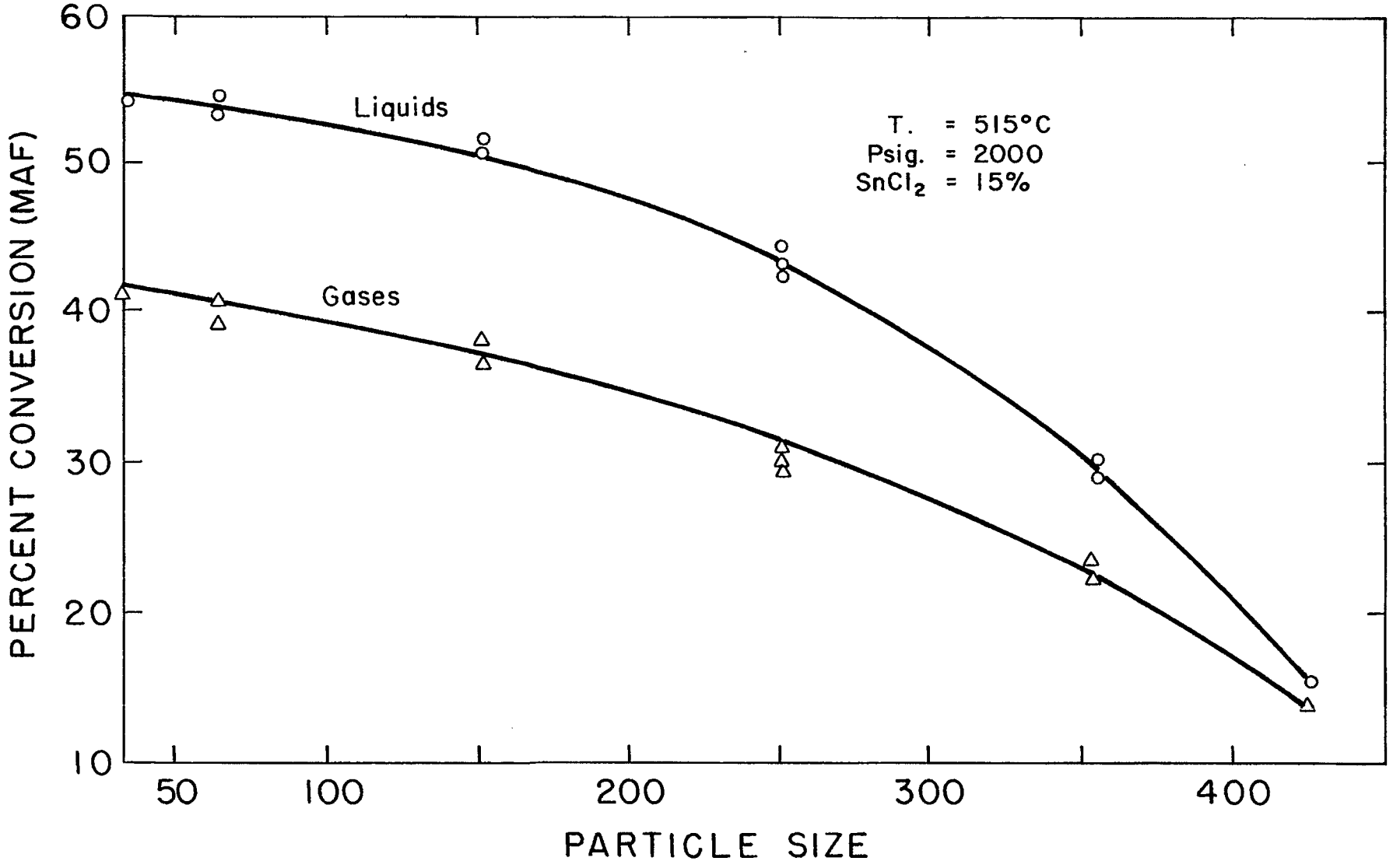


Figure 6. Spring Canyon coal, Particle Size vs. Liquid and Gases.

was controlled by the addition of coke. However, this represents a cost to the process in several ways (i.e. heat, throughput, handling and disposal). Therefore, the addition of starch as a water solution followed by drying and rescreening at a course size, has been used on subsequent work. This has been effective in rendering the charge free flowing. Another solution to the difficulty, where applicable, is the use of a course particle size, such as -40 mesh or greater. This material can normally be fed with no difficulty and no pretreatment.

The second major problem in the operation of the reactor, as also indicated previously, is that coal particles which strike the hot walls tend to stick, be devolatilized and form coke. This process, if continued, results in bridging in the reactor. In the two inch diameter reactor hot zone this sticking tendency limits the feed charge to 200-300 grams. The continuous hydrogenation reactor then becomes actually a batch reactor.

A study of the parameters affecting the sticking tendency revealed that coke addition did not alleviate the situation. Figure 7 (Table VI, Appendix A) demonstrates this where various ratios of coal to coke were used with no catalyst added. The upper portion of this figure shows the percentage distribution of reacted solids in three zones of the reactor. These zones are the quench tank, the hot zone and intermediate area between the hot zone and the quench tank. The addition of coke to the charge does cause somewhat more solids to reach the quench tank, but this is actually more coke, not more coal. The percentages retained in the hot zone and in the intermediate zone are independent of the amount of coke added. A division was made between that retained in the hot zone and that in the intermediate zone because of the difference in character between the two materials. That retained in the hot zone is very hard, completely devolatilized and very difficultly removed from the reactor. That sticking in the intermediate or "between" zone is moist with hydrogenation liquids, only lightly held to the walls and very easily removed. Since the addition of coke was found to be ineffectual in preventing bridging in the reactor and unnecessary to prevent bridging in the hopper, its use was discontinued.

The original design of the reactor contained a thermal well, used during the course of the Spring Canyon coal study to measure temperatures in the reaction zone. This thermal well is a one-half inch tube that extends the length of the reactor from the top. Its presence provided more surface for the coal to adhere to and bridging occurred more readily with it in place. Because of this the thermal well was removed and temperature measurements were made by the use of thermocouples placed on the outer surface of the reactor walls. The removal of the thermal well did serve to decrease the build up of solids in the reactor but the build up was still sufficient to give complete bridging for samples of 400 grams or more.

Tests made on the temperature and time of drying of coal charges prior to their insertion into the hopper led to a useful pretreatment technique. This study indicated that a surface oxidation of the coal particles is successful in reducing the portion of solids that remain in the hot zone following a trial. Figure 8 (Table VII, Appendix A) shows the results for drying coal charges for various time periods at 110°C. The percentage of

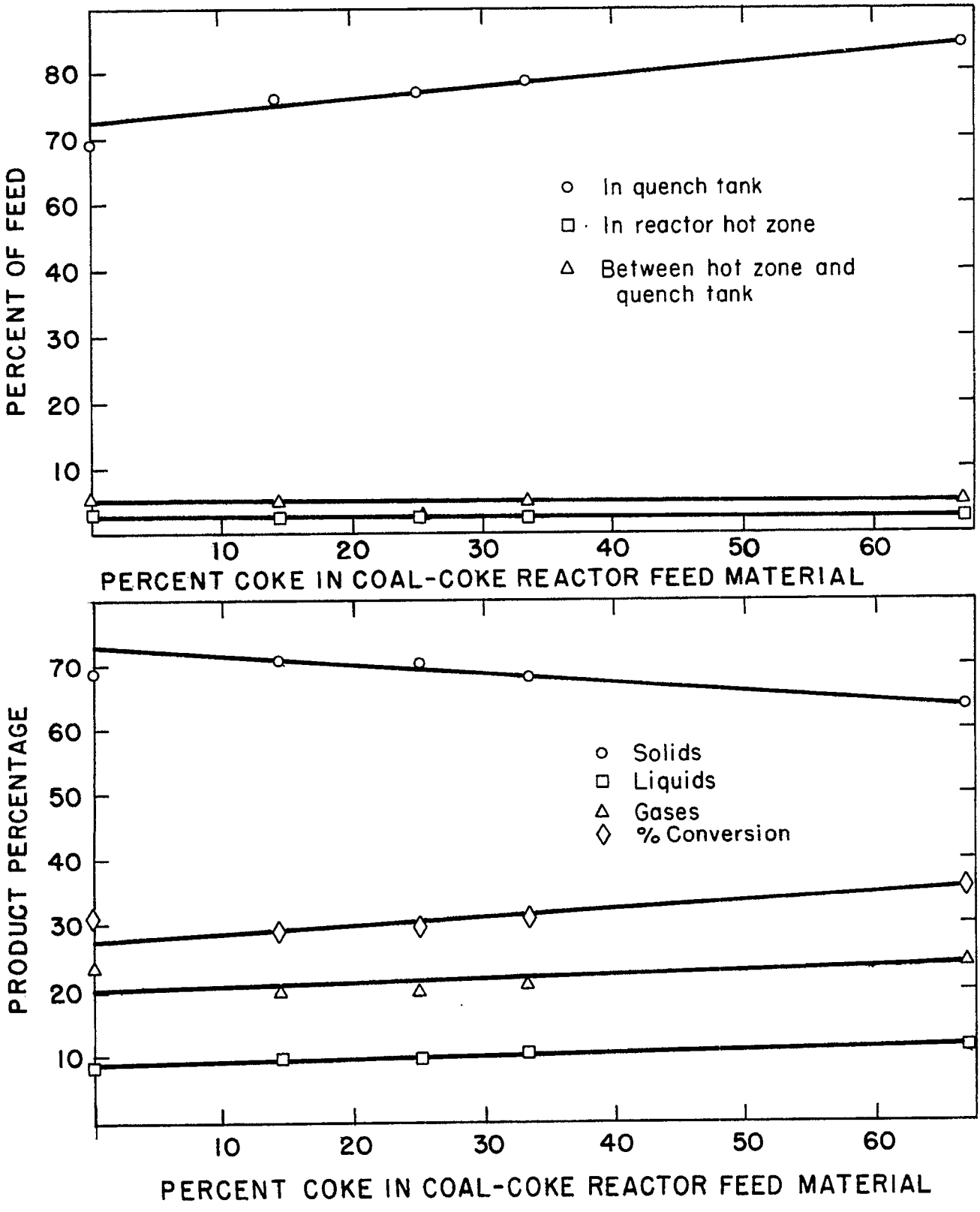
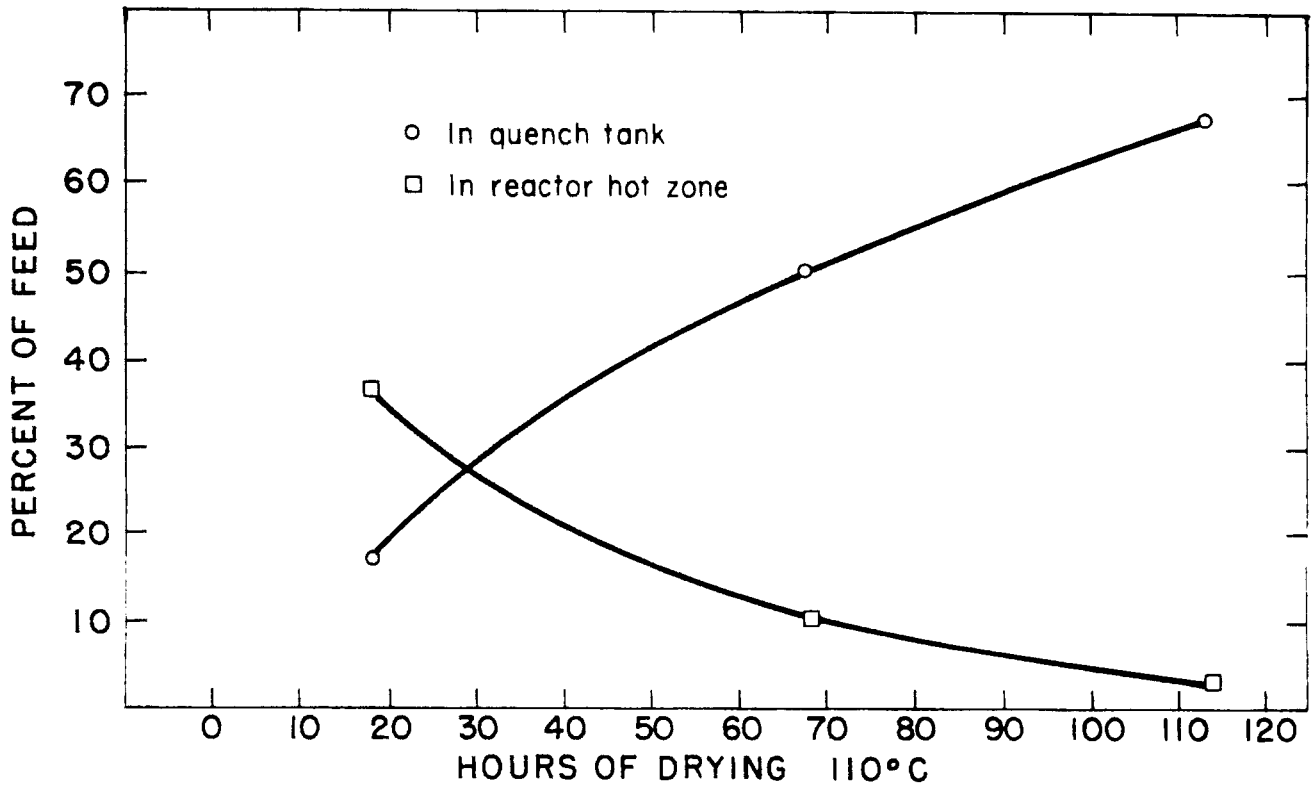


Figure 7a. Distribution of solid products.

Figure 7b. Distribution of reaction products.



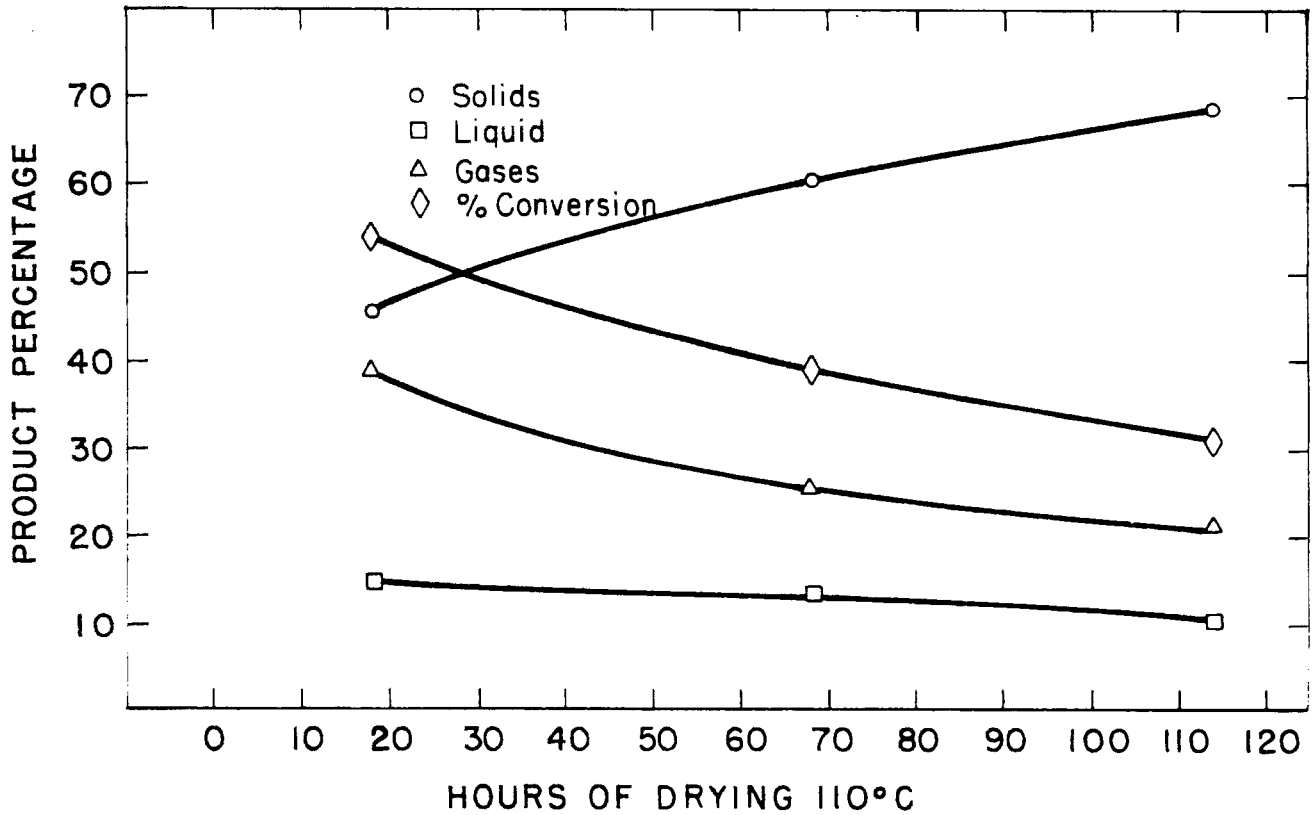


Figure 8a. Distribution of solid products. Drying time at 110°C.

Figure 8b. Distribution of reaction products. Drying time at 110°C.

solids retained in the hot zone falls off rapidly with extended drying periods. However, as shown in the lower portion of this figure, conversion, gases, and liquids fall off rapidly while solids increase rapidly with the longer drying times.

The temperature of drying is extremely important as shown in Figure 9 (Table VIII, Appendix A). The upper portion shows that the percent of solids retained in the hot zone drops from 37 to 5 percent for 18 hours of drying at 128°C from that for the same time at 110°C. However, the lower portion of this figure shows that the percent conversion, liquids and gases fall off rapidly with long drying periods. For -100 mesh coal the optimum condition was chosen at 18-24 hours drying at 128°C. Longer drying periods at this temperature produced no difference in any of the parameters measured, as shown by Figure 10 (Table IX, Appendix A).

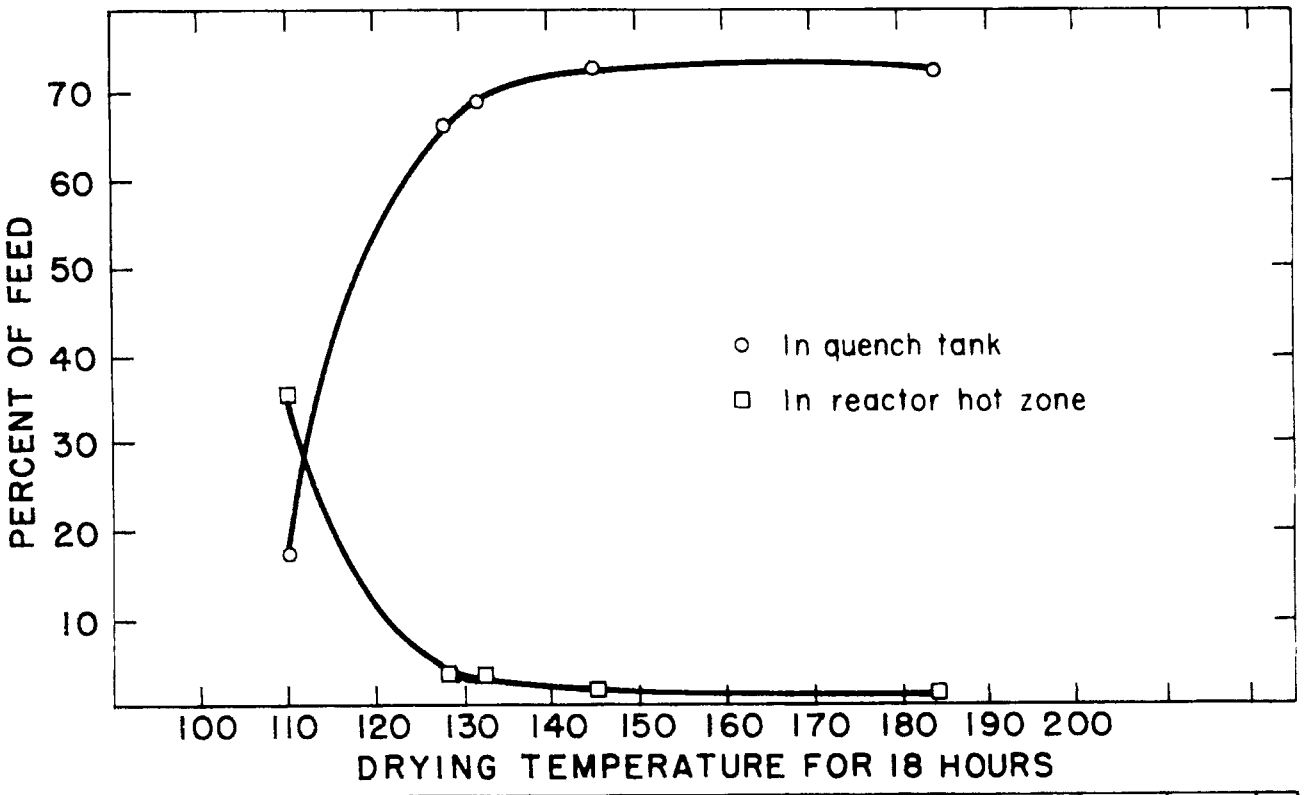
With this basis for charge preparation, 128°C for 18 to 24 hours, -100 mesh, and one percent starch it was possible to study the effects of catalyst, catalyst concentration, feed rate, and temperature on conversion and product formation.

A study of feed rate was made, using Coalville, Utah coal. This is a subbituminous coal with little or no coking character. This coal was chosen because its lack of coking character was expected to render it less likely to stick in the reactor hot zone. A catalyst to coal ratio of approximately 0.09 to 0.11, using $SnCl_2 \cdot 2H_2O$ was used. This ratio is defined as the weight of Sn divided by the weight of dry, ash-free coal in the feed charge. A temperature of 557°C and a pressure of 2000 psi H_2 were used.

Figure 11 (Table X, Appendix A) shows the result of this study, where feed rates of 5, 20, 35 and 50 grams per minute were used. A duplicate determination was made at 5 grams per minute. Conversion falls off slightly at high feed rates. Liquid production decreases markedly at 20 grams per minute but improves at higher rates. Gas production increases for 20 and 35 grams per minute but falls off again at 50 grams per minute. Because of the loss of conversion and loss in liquid production, as well as the increase in gas production, subsequent tests were conducted at the 5 gram per minute feed rate.

The effect of varying catalyst concentration is shown in Figure 12 (Table XI, Appendix A). The reaction conditions were 578°C, 2000 psi, 5 g/m, with -100 mesh Coalville coal that had been dried for 18 hours at 128°C. The concentration of catalyst seems to have very little effect on solids distribution but a very marked effect on product distribution. A Sn/Coal ratio in the neighborhood of 0.10 was chosen for the comparison of coals.

Three different coals were carefully compared using $SnCl_2 \cdot 2H_2O$ as the catalyst. These coals were Coalville, Utah (subbituminous), Hiawatha, Utah (bituminous) and Assam, India (bituminous). Proximate and ultimate analyses on these coals are shown in Table II. Hydrogenation test data for the coals are given in Table III. These coals were hydrogenated at temperatures



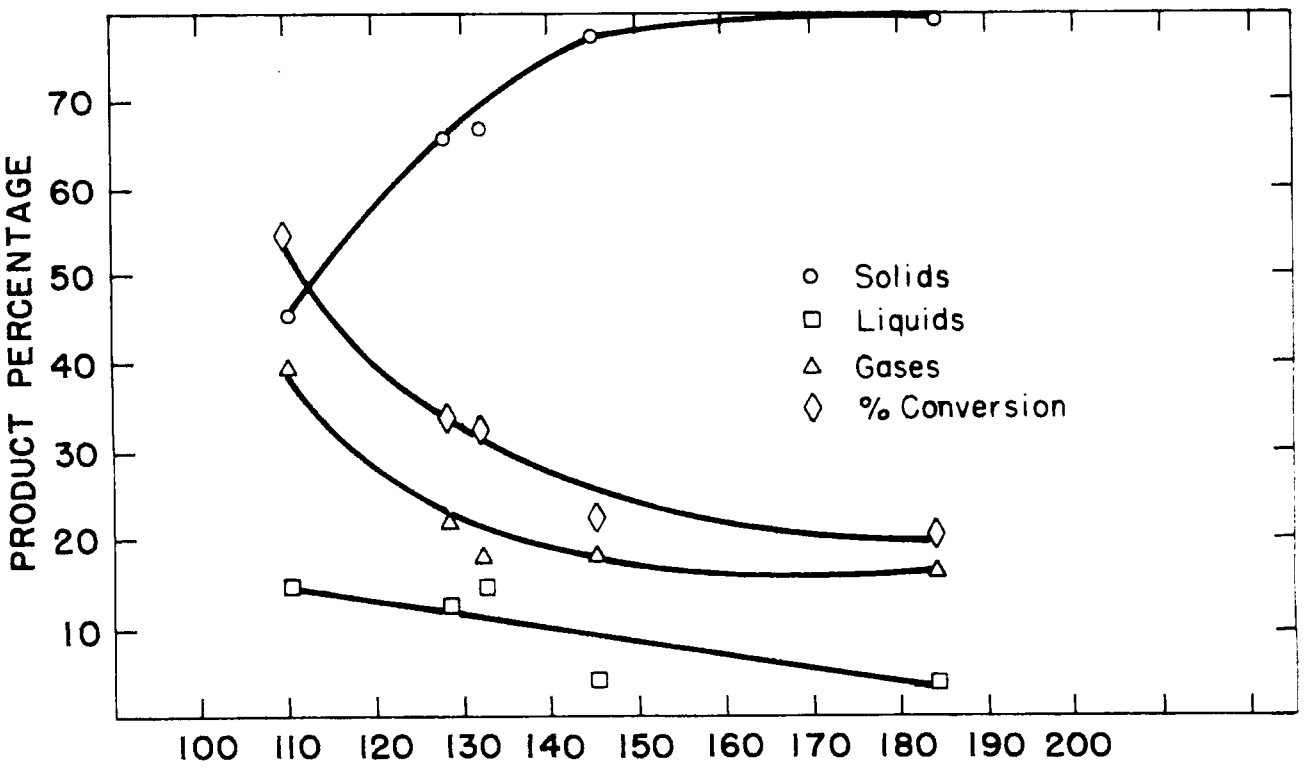
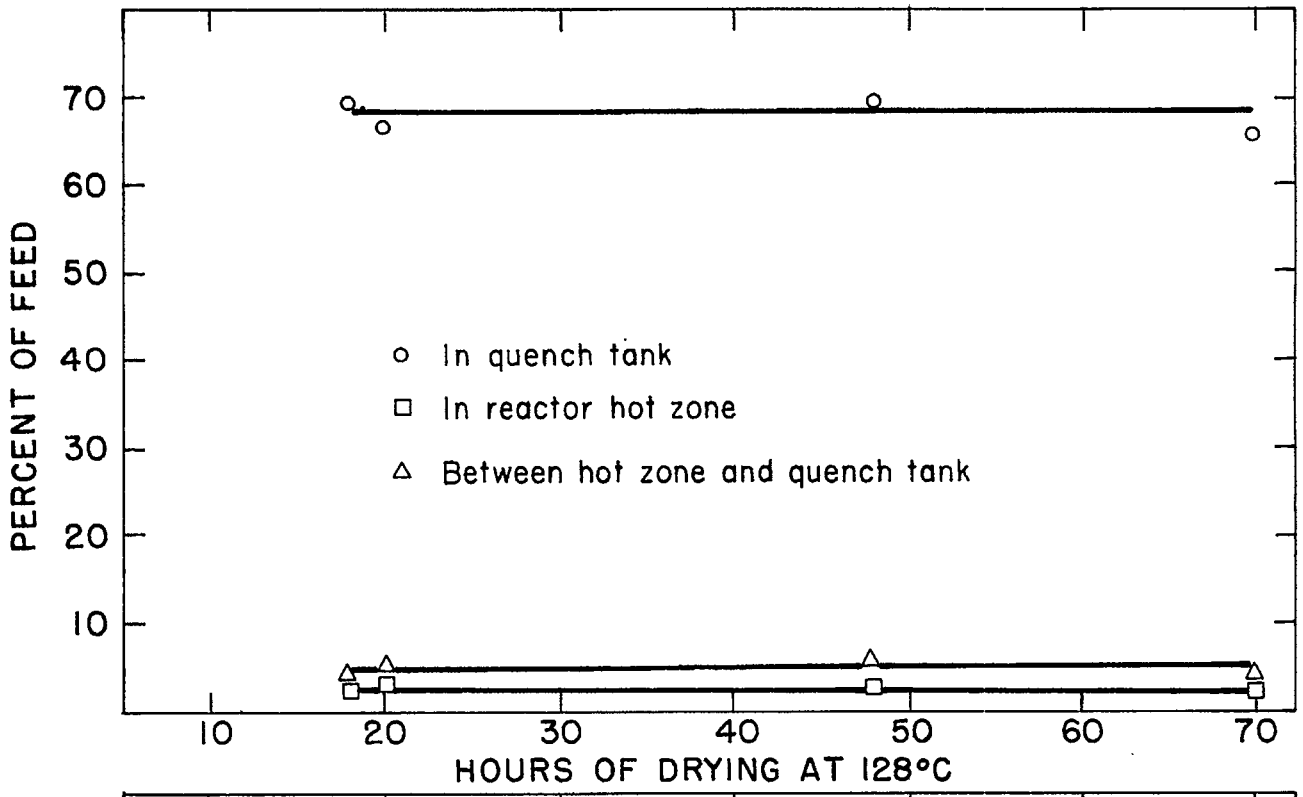


Figure 9a. Distribution of solid products.

Figure 9b. Distribution of reaction products.



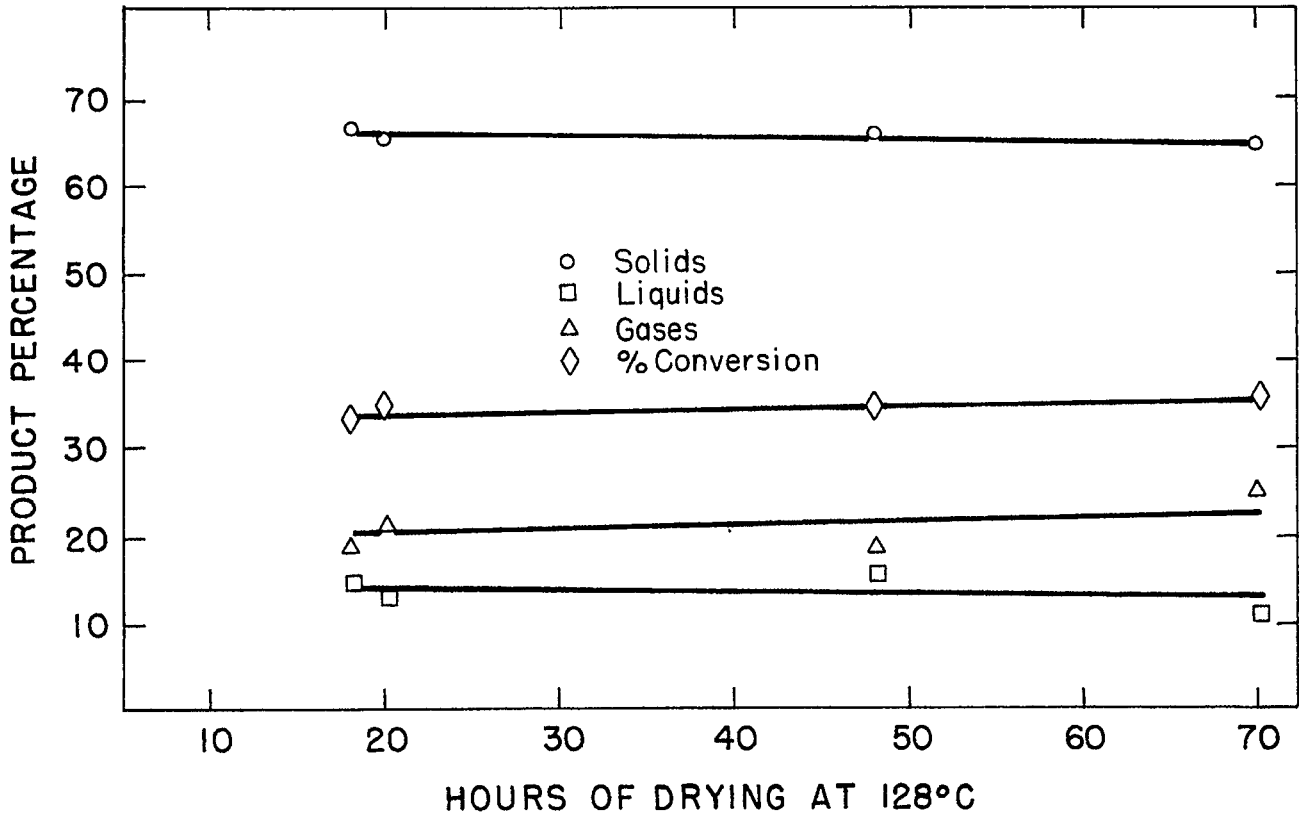


Figure 10a. Distribution of solids.

Figure 10b. Distribution of reaction products.

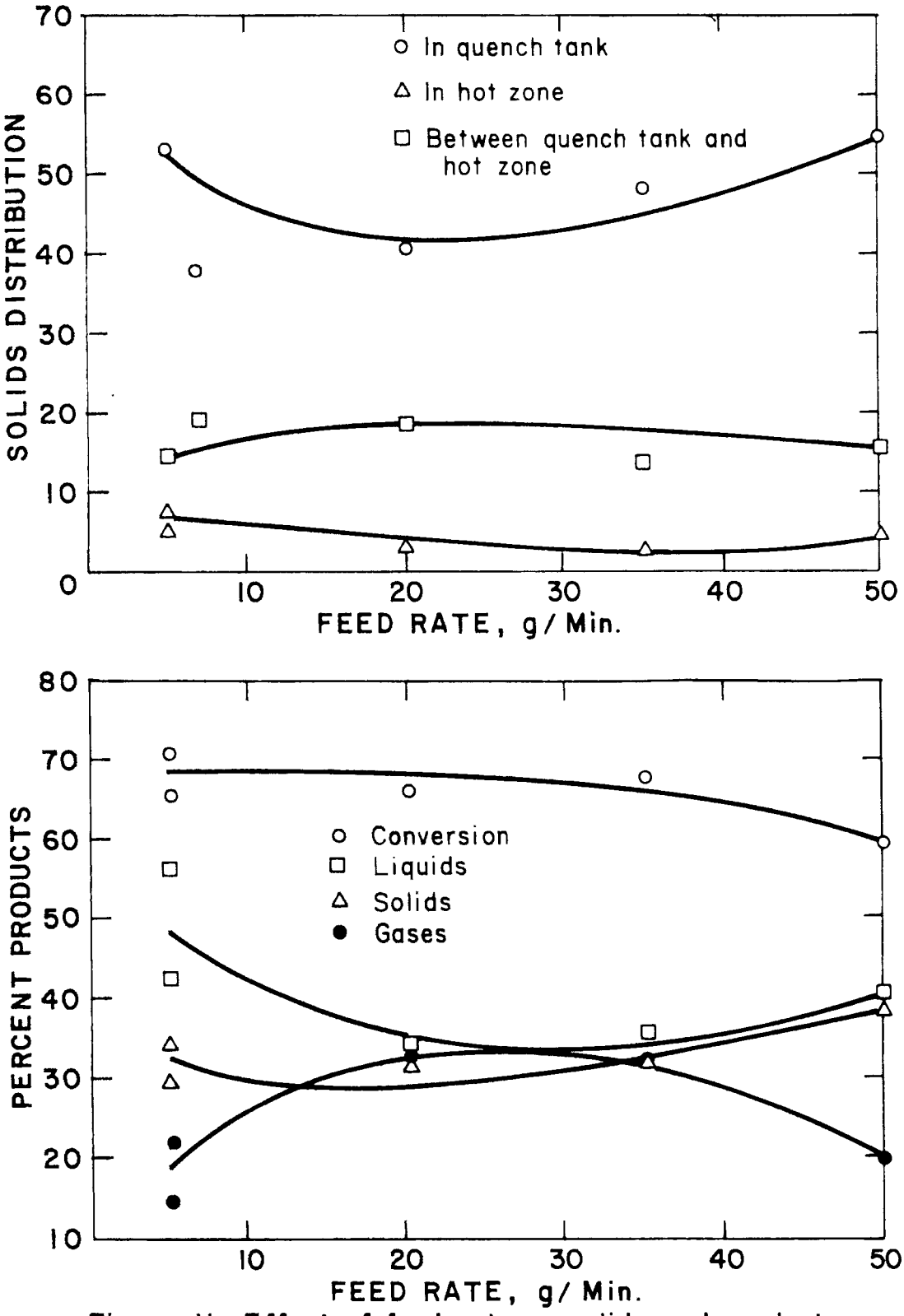
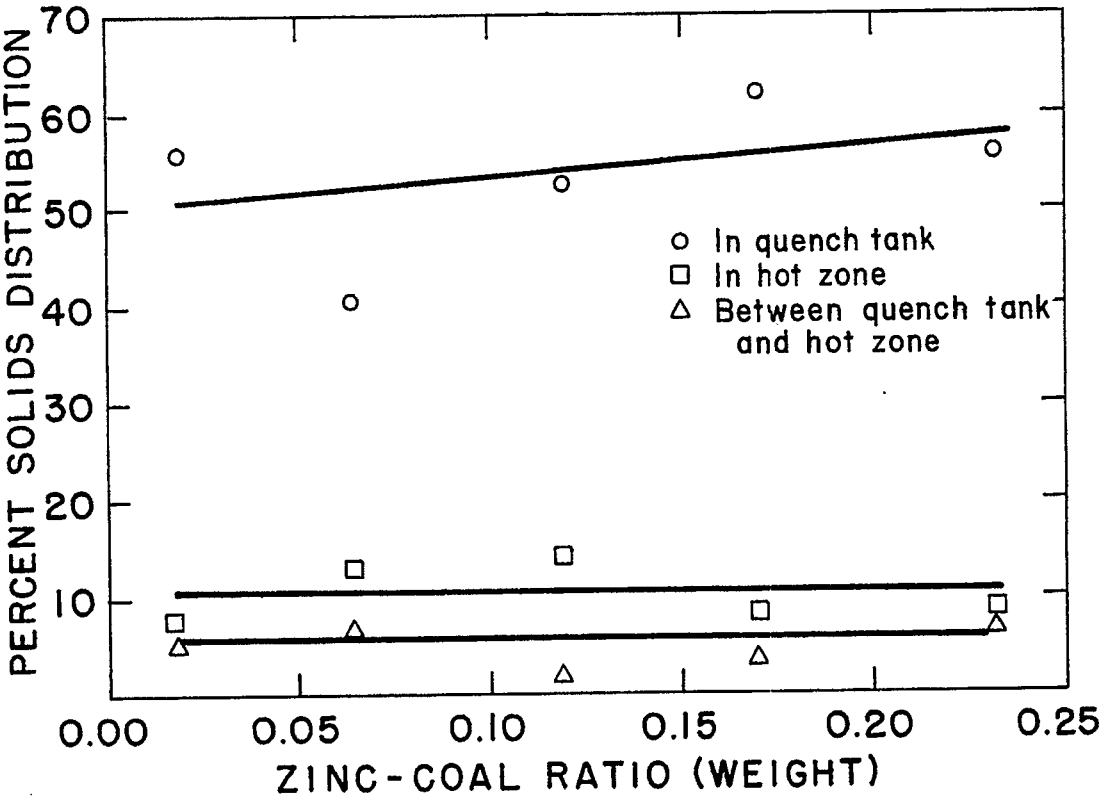


Figure 11. Effect of feed rate on solids and product distributions of Coalville, Utah coal.



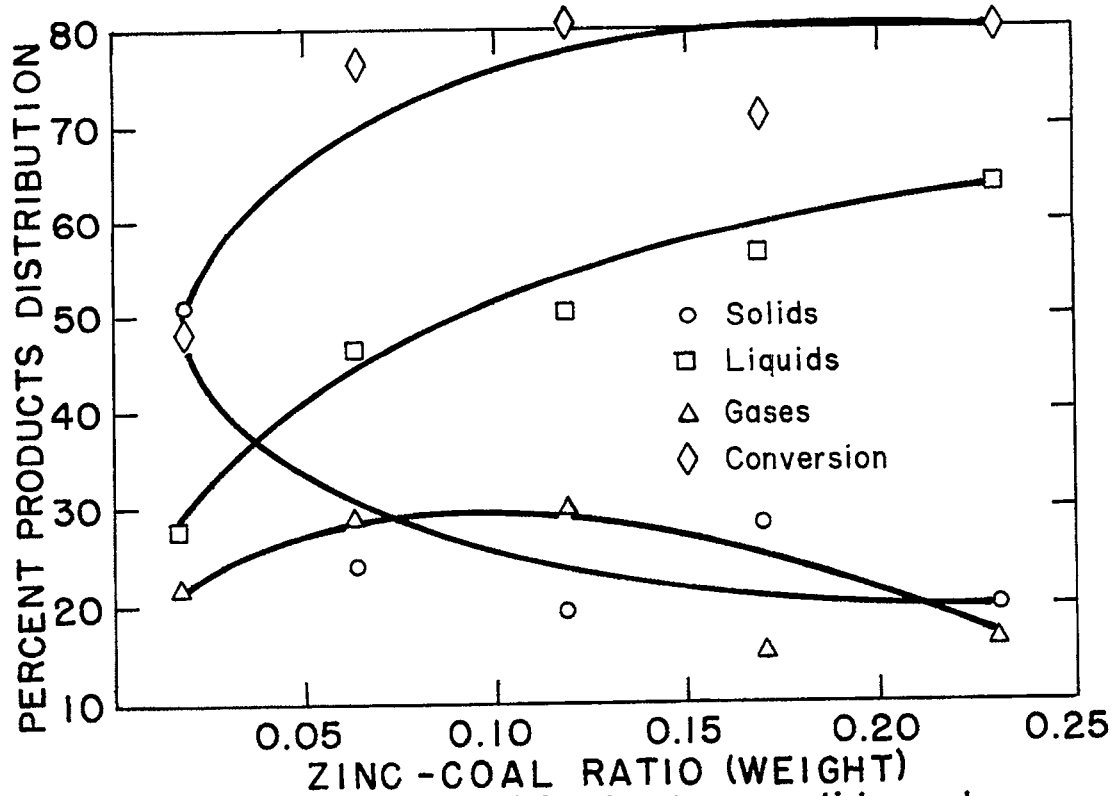


Figure 12. Effect of feed rate on solids and product distributions of Coalville, Utah coal.

from 475°C to 640°C at 2000 psi, 5 g/m, -100 mesh and dried for 20 to 24 hours at 128°C prior to hydrogenation.

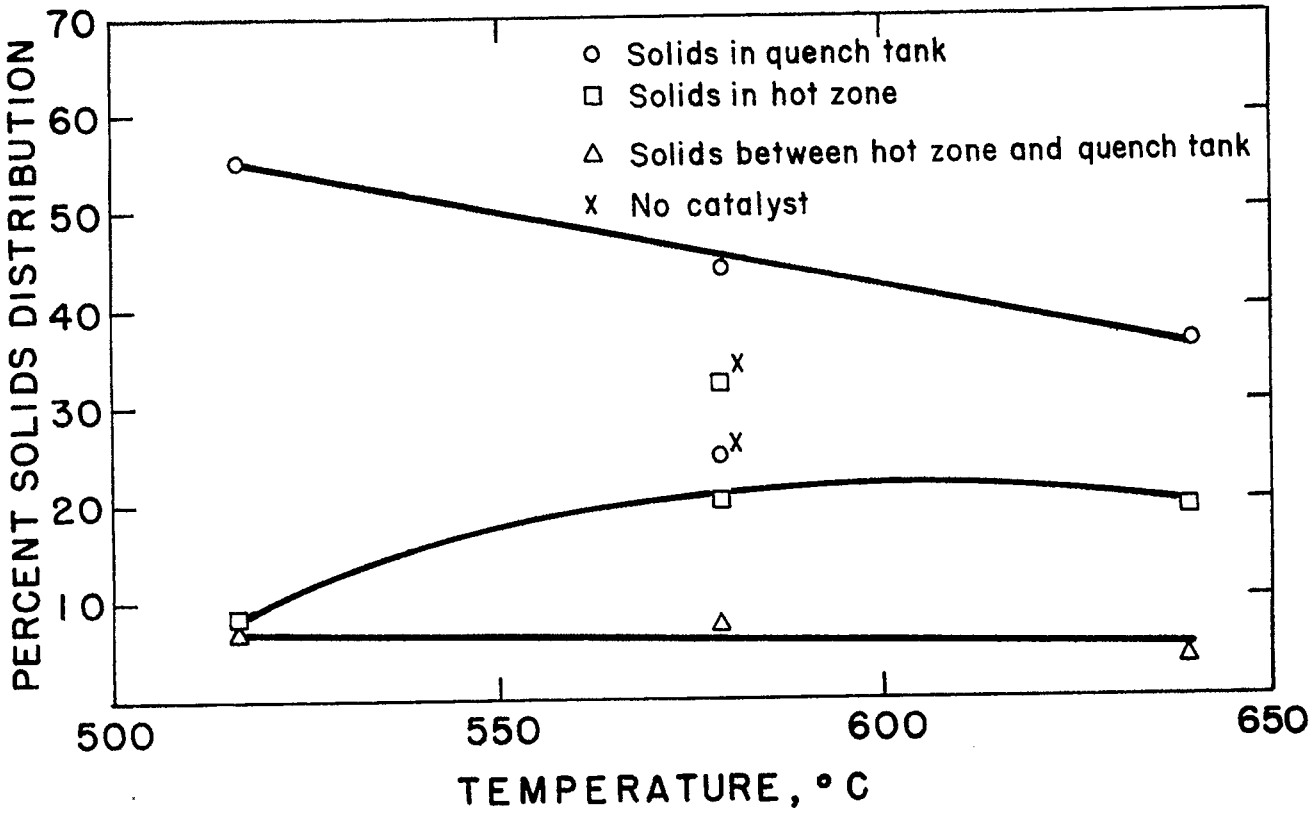
Figures 13, 14 and 15 show the data in visible form. Figure 13 is for Assam, India coal, Figure 14 is for Coalville coal and Figure 15 is for Hiawatha coal. The data shown in these figures is compiled in Tables XII, XIII and XIV, Appendix A. Actual comparison of the three coals is best seen in Figure 16. Here, the data for liquid and gaseous production and that for conversion for all three coals are shown together. An average curve was drawn through the total data, then a band of 5 percent variation drawn above and below the average curve. From this it is seen that almost all the data falls within this 10 percent range. All three criteria show increase with temperature to about 570°C. Liquid production falls off at higher temperatures. Gas production at higher temperatures increases sufficiently to make the conversion percentage continue to climb, but at a less rapid pace.

Average values for the tests run on the three coals are collected in Table XV, Appendix A. Although the averages are too close together to be certain that one is greater than another, the Coalville coal does average a few percentage points higher than Hiawatha in liquid production, with Assam falling between. Hiawatha coal produces slightly more gas than Coalville and the Assam coal is about equal to Hiawatha. Also, the conversion of Assam coal is the higher of the three, on the average. More detailed duplication of data would be required to be certain of this conclusion.

An examination of the solids distribution curves indicates that the Assam coal tends to stick more in the hot zone of the reactor than do the other coals. However, it is possible that a more appropriate technique of coal preparation would result in less sticking.

The use of tin compounds as catalysts in the hydrogenation of coal and coal tar has a long history as evidenced by the literature. However, tin compounds are expensive, difficult to apply effectively to the coal surfaces, the chlorides are particularly corrosive and the recovery of the tin from the solid residue is difficult. All these problems are accentuated in connection with the free-fall reactor since large amounts of catalyst are required.[7] Consideration of these items has led others to seek out alternate catalysts[7].

The use of $ZnCl_2$ as a hydrogenation catalyst has some obvious advantages with respect to $SnCl_2 \cdot 2H_2O$. It is readily water soluble and is easily applied to coal. $SnCl_2 \cdot H_2O$ must be dissolved in HCl or an organic solvent for treating the coal. When the coal is dried, HCl is evolved. This is expensive in that the acid itself represents a cost, it is corrosive and would require equipment and expense for recovery. The $SnCl_2 \cdot H_2O$ is converted in the drying process to a hydroxy chloride, perhaps $Sn_4(OH)_6Cl_2$ or $Sn_3(OH)_4 \cdot Sn(OH)_2Cl_2$ and is not readily recoverable even with strong HCl. On the other hand, $ZnCl_2$ is water soluble, is not altered in the coal drying or reactor processes and can be more readily recovered from the coal residue after reaction.



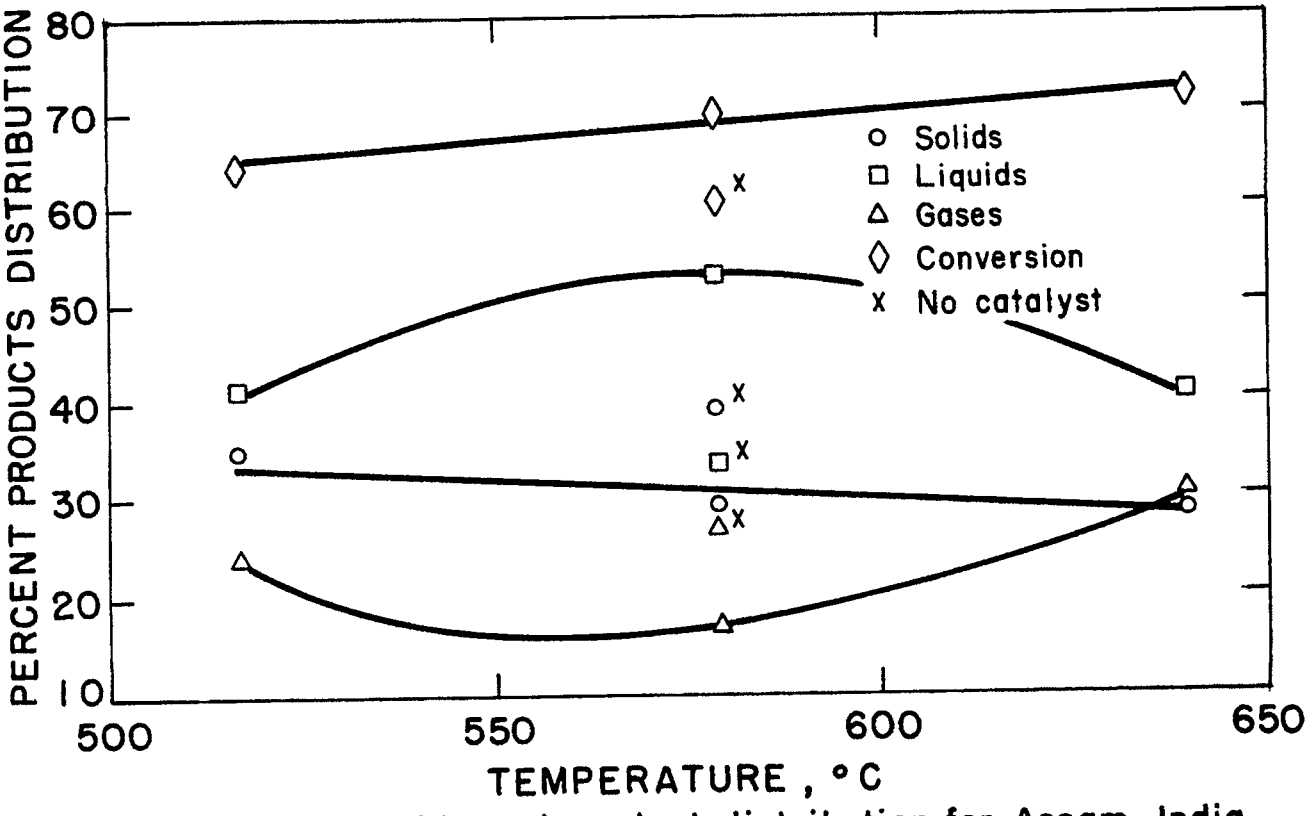
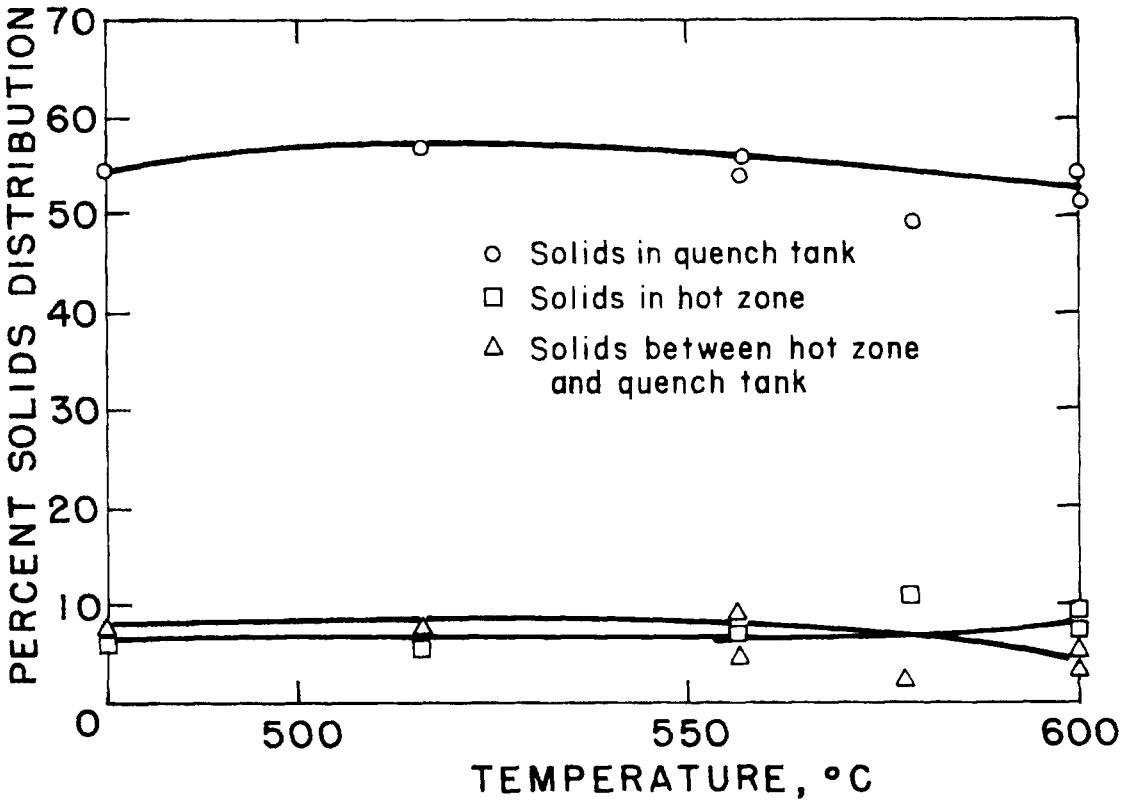


Figure 13. Solids and product distribution for Assam, India coal at three hydrogenation temperatures.



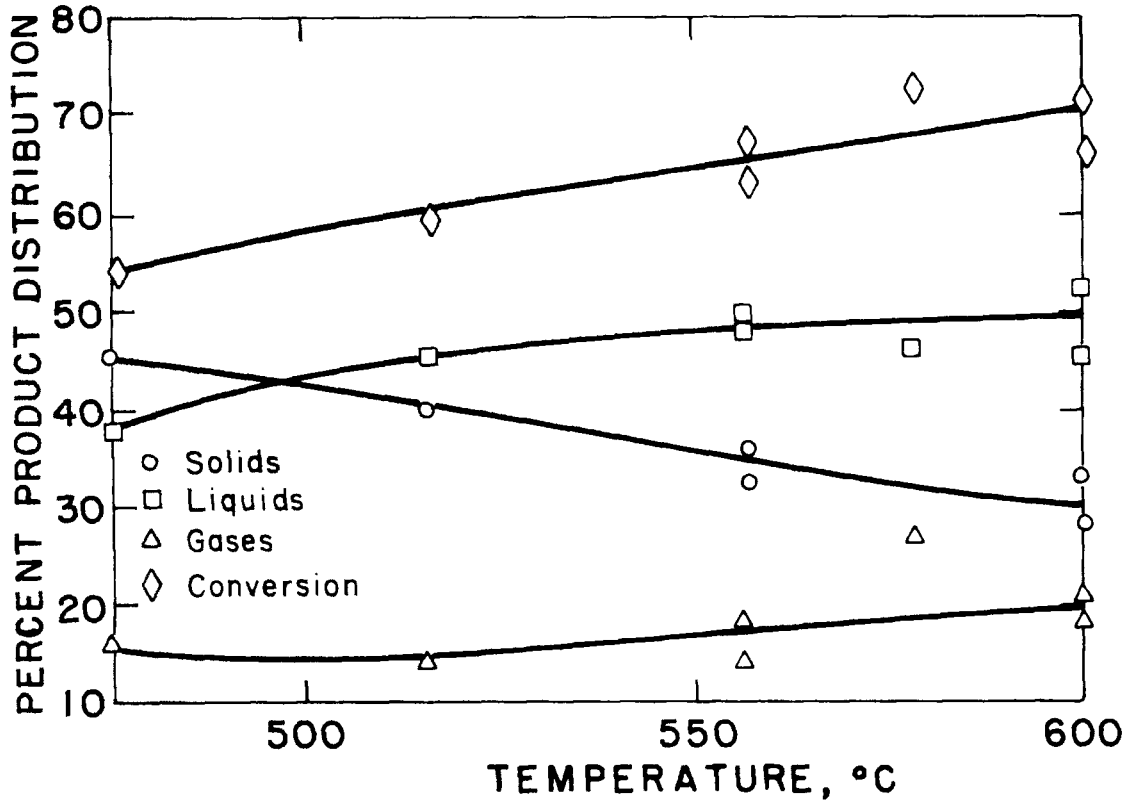
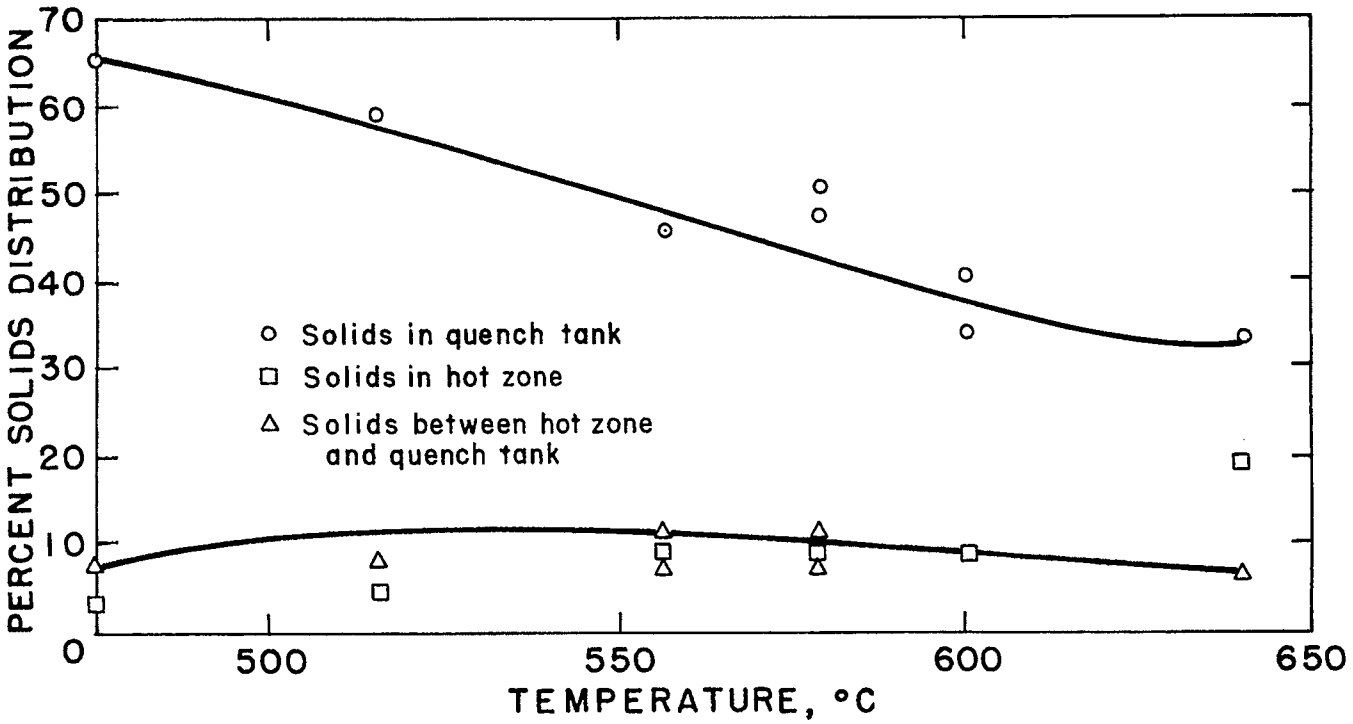


Figure 14. Solids and product distributions for Coalville, Utah coal as a function of hydrogenation temperature.



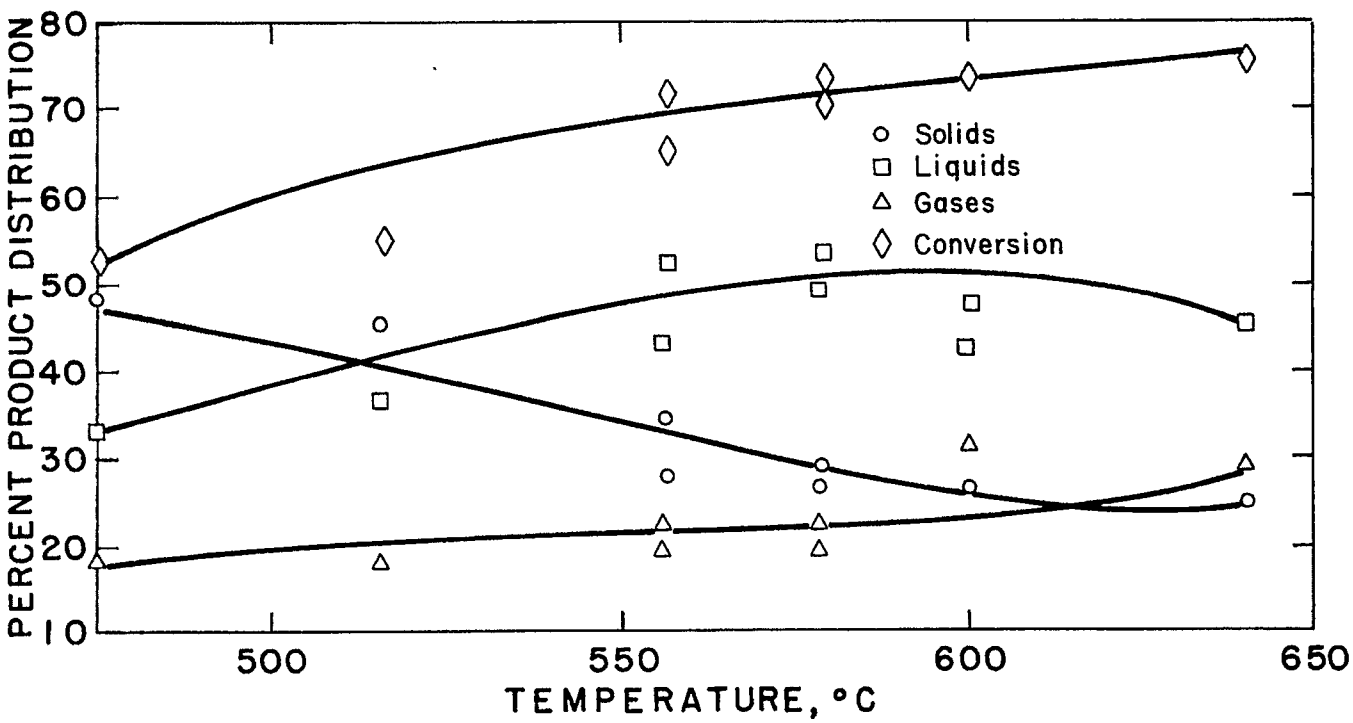


Figure 15. Solids and product distributions for Hiawatha, Utah coal as a function of hydrogenation temperature.

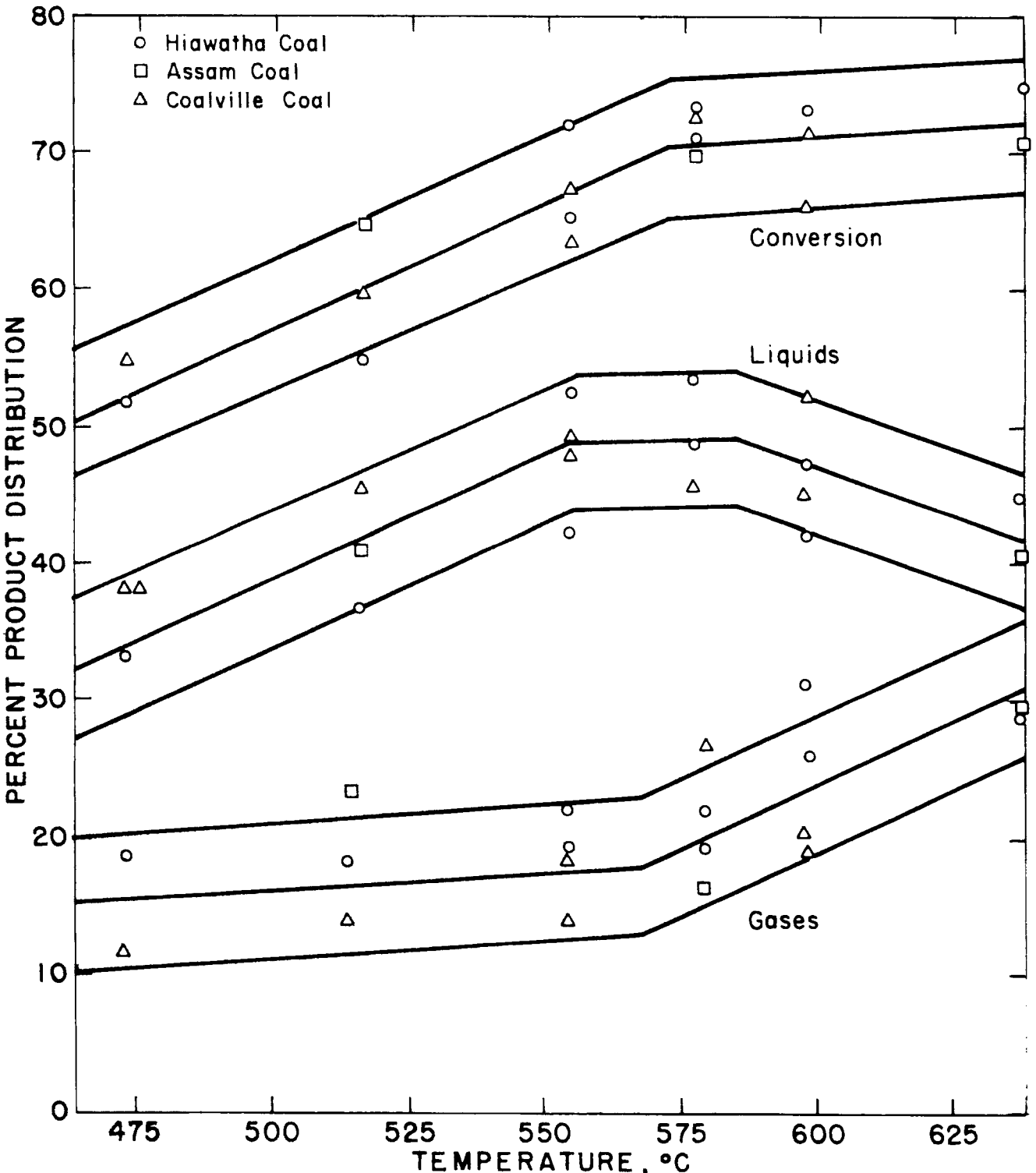


Figure 16. Comparison of Assam, Coalville and Hiawatha coals with respect to hydrogenation at various temperatures.

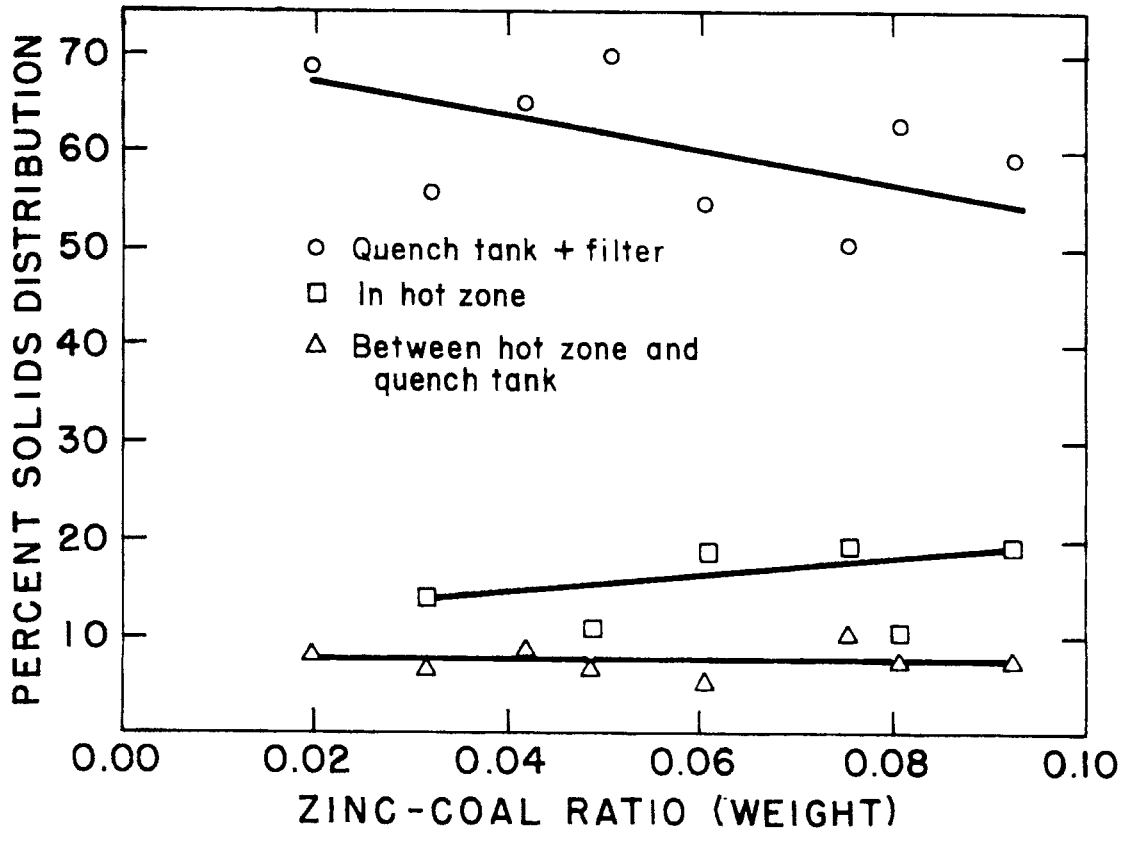
In consideration of these factors, a series of trials was made to measure the effectiveness of $ZnCl_2$ as a hydrogenation catalyst and to discover the amount required for best results. Figure 17 (Table XVI, Appendix A) shows the solids distribution and the product distribution for samples of Coalville coal, -40 mesh, with varying amounts of $ZnCl_2$ added. In each case, hydrogenation was done at 2000 psi, 578°C, 5 g/m and 60 liters of H_2 per minute gas flow. The Zn to coal (dry ash free basis) was varied from 0.02 to 0.09.

The varying amount of $ZnCl_2$ seems to have little effect on solids distribution although slightly more solids are retained in the hot zone with higher amounts of catalyst. Also, less solids pass through the hot zone with higher amounts of catalyst, but this is related to the increased conversion. The coal conversion line seems to reach a peak in the area of 0.05 to 0.06 Zn/coal ratio. Likewise the liquids production is a maximum at this point and gas production is only slightly above its minimum. This conclusion means that $ZnCl_2$ has an additional advantage to those previously mentioned, that of requiring only half the concentration needed for $SnCl_2 \cdot 2H_2O$. It is apparent upon examination, that the yields on conversions are higher by 2-3 percent for the tin salt so the advantage is not all on the side of using $ZnCl_2$.

A coal particle size study was made using $ZnCl_2$ as the catalyst in an effort to determine whether or not the coal pretreatment steps could be simplified. Figure 18 shows the results obtained on a series of Coalville coal samples at different upper size limits. For this work, samples were ground to -10, -20, etc. mesh sizes in order to have the results reflect the use of all the coal. Better results could be expected if the fines were rejected beyond a selected particle size, but this could represent a formidable loss in the economics of the process. In Figure 18 (Table XVII, Appendix A), the data was collected with approximately 0.07 Zn/coal ratio, 578°C, 5 g/m and 60 liters/min gas flow.

In this study it is apparent that little difference is found for finer particle sizes. Samples of -20 mesh are equal in yield to -100 mesh. The fine sizes do seem to produce more liquid and less gas. The fine sizes also seem to stick less in the hot zone of the reactor. With these observations a particle size of -40 or -60 mesh would seem to be most suited for use with $ZnCl_2$.

In overall perspective, the studies with the continuous hydrogenation reactor have been optimistic with respect to conversion of coals, as especially with respect to liquids production. The change to $ZnCl_2$ as a catalyst has shown many advantages and will be continued.



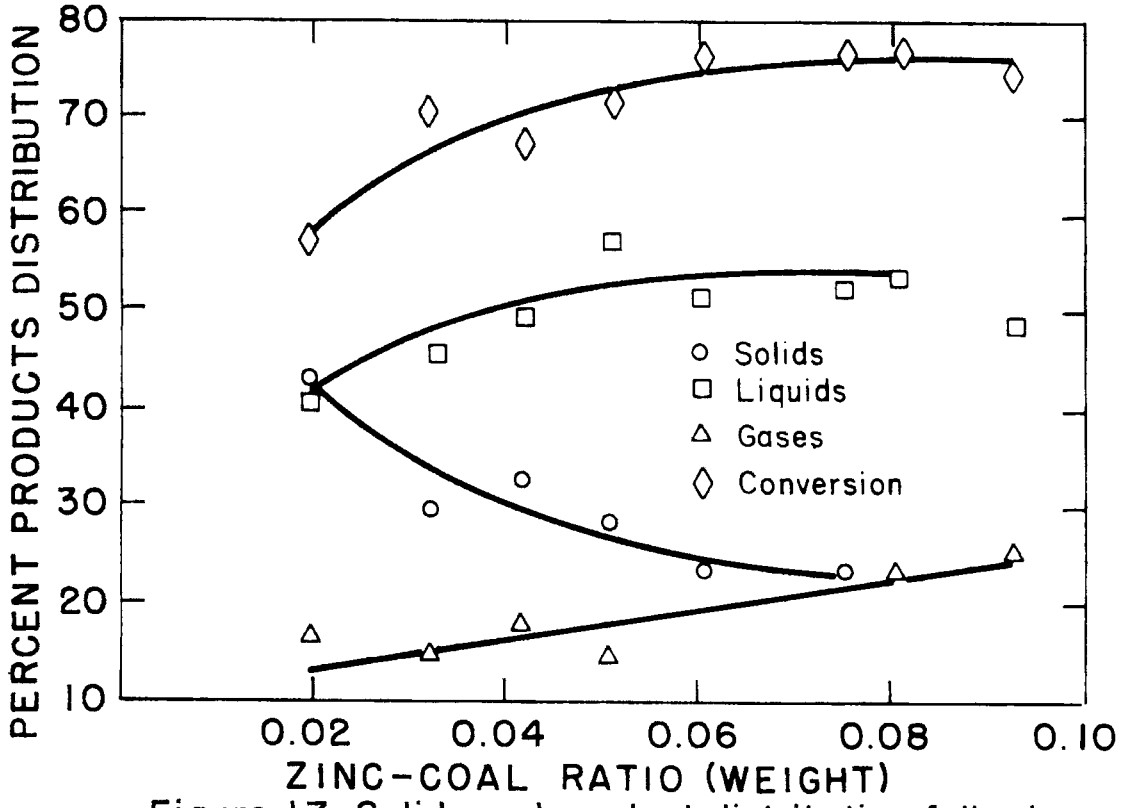
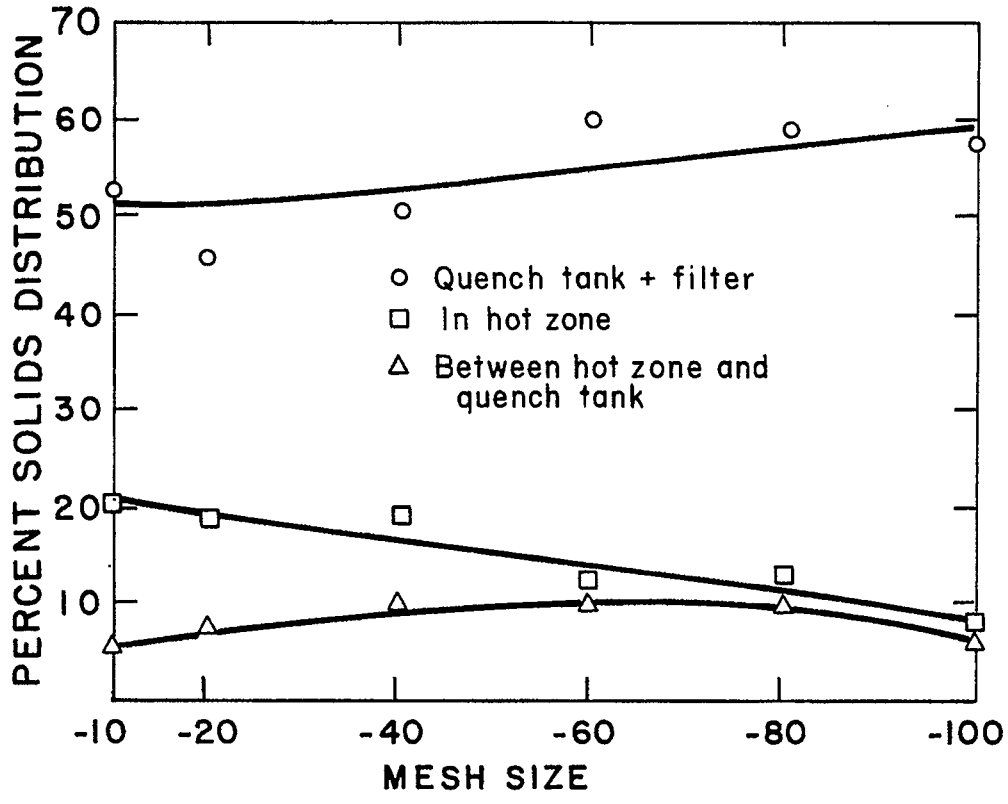


Figure 17. Solids and product distribution following hydrogenation of Coalville, Utah coal using zinc chloride as the catalyst.



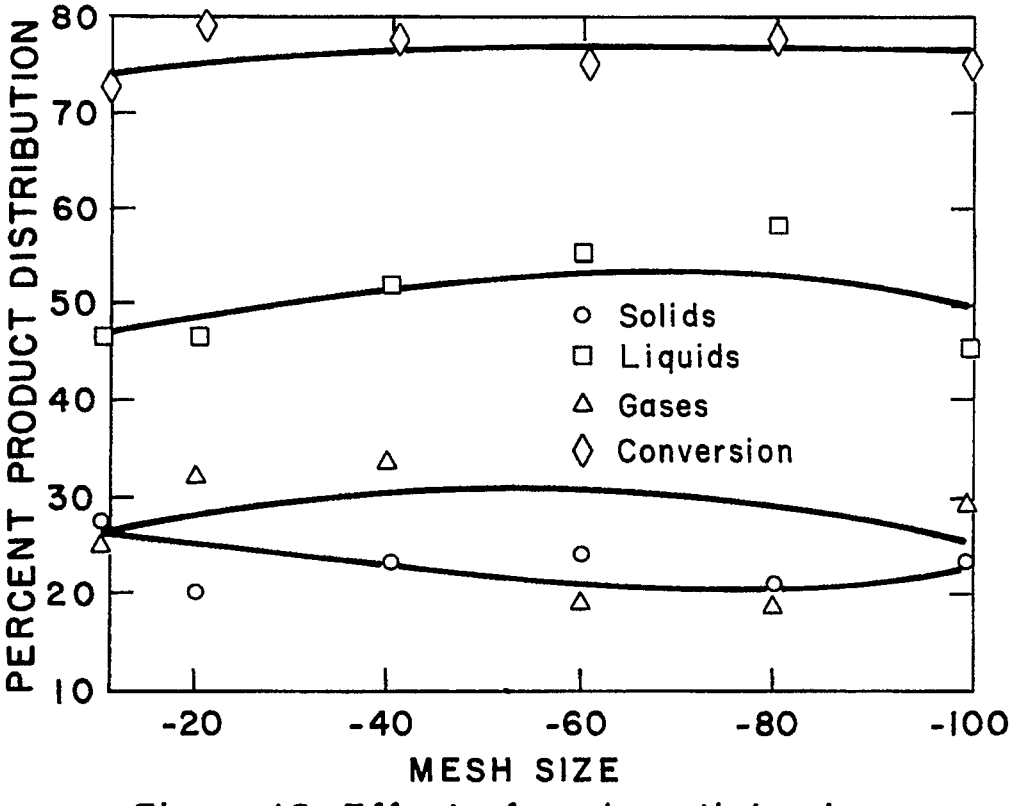


Figure 18. Effect of coal particle size on solids and product distribution following hydrogenation.

APPENDIX A

TABLE I

DATA SHOWN IN FIGURE 3

SPRING CANYON COAL-TEMPERATURE VERSUS CONVERSION

Test Number	Temperature	Percent Conversion	Percent Asphaltene	Percent Liquids	Percent Gas
1	400	39.3	18.4	23.2	16.1
2	450	52.3	24.0	31.3	21.0
2a	450	54.0	--	33.0	21.0
3	515	74.2	30.5	44.5	29.7
3a	515	74.0	--	45.0	29.0
3b	515	72.6	29.2	42.7	29.9
5	600	74.9	21.1	34.1	40.8
6	625	73.8	19.3	30.6	43.2
6a	625	76.0	--	32.6	40.5
7	715	75.2	13.7	26.6	48.6

Sample: Spring Canyon Coal

Size: 40-80 mesh

Catalyst: 15 percent $SuCl_2 \cdot 2H_2O$

Ratio: 1:1 Coal to Coke

Hydrogen Pressure: 2000 psi

Feed Rate: 5 g/min

Appendix A

TABLE II

DATA SHOWN IN FIGURE 4

SPRING CANYON COAL-HYDROGEN PRESSURE VERSUS PERCENT CONVERSION

Test Number	H_2 Pressure Psi	Percent Conversion	Asphaltene	Liquids	Gases
27	500	43.0	--	19.0	24.0
28	1000	58.2	22.9	28.2	30.0
28a	1000	56.8	--	29.1	27.7
29	1500	69.0	--	38.1	30.9
29a	1500	67.6	--	37.1	30.5
30	2000	75.0	26.0	43.0	32.0
30a	2000	72.1	26.0	44.0	28.1
30b	2000	73.8	--	45.2	28.6
32	2500	75.0	--	45.0	30.0
33	3200	75.5	29.2	44.5	31.0
33a	3200	75.6	--	46.7	28.9
11	3000	75.0	--	43.6	31.4

Sample: Spring Canyon Coal

Size: 40-80 mesh

Catalyst: 15% $SuCl_2 \cdot 2H_2O$

Ratio: 1:1 Coal to Coke

Temperature: 515°C

Feed Rate: 5 g/min.

APPENDIX A

TABLE III

VARIATION OF CATALYST CONCENTRATION

FIGURE 5

Test Number	Catalyst	Percent Conversion	Asphaltene	Liquids	Gases
40	0	44.3	15.0	20.3	24.0
41	7.5	60.0	--	36.0	24.0
42	15	74.1	30.0	44.0	30.1
42a	15	74.0	--	45.0	29.0
3	15	74.2	30.5	44.5	29.7
43	18	75.7	--	45.0	30.7
44	20	73.9	27.7	43.8	30.1
45	30	75.3	26.8	43.8	30.5
45a	30	76.0	--	46.0	30.0

Sample: Spring Canyon Coal

Size: 40-80 mesh

Catalyst: $SuCl_2 \cdot 2H_2O$

Ratio: 1:1 Coal to Coke

Temperature: 515°C

Pressure: 2000 psi H_2

Feed rate: 5 g/min.

APPENDIX A

TABLE IV

PARTICLE SIZE

Test Number	Particle Size (Microns)	Percent Conversion	Percent Liquids	Percent Gases
56	420	31.3	16.3	15.0
57	355	51.5	29.0	22.5
57a	355	53.7	30.1	23.6
30	250	75.0	43.0	32.0
30a	250	74.2	44.5	29.7
30b	250	74.0	45.0	29.0
58	150	87.2	50.2	37.0
58a	150	89.2	51.5	38.2
59	60	93.0	53.0	40.5
59a	60	93.8	54.5	39.3
60	40	95.0	54.0	41.0

Sample: Spring Canyon Coal

Size: 40-80 mesh

Catalyst: 15 percent $SuCl_2 \cdot 2H_2O$

Ratio: 1:1 Coal to Coke

Temperature: 515°C

Pressure: 2000 psi

Reed Rate: 5 g/min.

APPENDIX A

TABLE V

HYDROGENATION OF SOME WESTERN COALS

Test Number	Coal Sample	Percent Conversion	Liquids	Asphaltene	Gases
3	Spring Canyon	74.2	44.5	30.5	29.7
4	Spring Canyon	72.6	42.7	29.2	29.9
65	Kaiparowits (Spencer Mine)	77.3	45.3	23.2	32.0
66	Alton	77.3	44.3	28.1	33.0
67	Kaiparowits (Last Chance Creek)	74.6	45.6	29.6	29.0
68	Hiawatha	76.1	44.5	30.0	31.6
69	Big Horn (No catalyst)	16.7	7.0	--	9.7
70	Big Horn	61.0	34.0	22.0	27.0
71	Big Horn (No coke)	60.9	32.8	--	28.1

Size: 40-80 mesh

Catalyst: $SuCl_2 \cdot 2H_2O$

Ratio: 1:1 Coal to Coke

Temperature: 515°C

Pressure: 2000 psi

Feed Rate: 5 g/min.

APPENDIX A

TABLE VI

SOLIDS-PRODUCT DISTRIBUTION WITH COAL:COKE MIXTURES

Figure 7

Test Number	Percent Coke	Solids Distribution Percent			Product Distribution, Percent			
		Wet	Dry	Between	Solids	Liquids	Gases	Conversion
67	86.7	84.1	2.8	5.2	63.9	11.5	24.6	36.1
70	33.3	79.4	2.6	4.6	68.8	10.6	20.6	31.2
71	25.0	77.8	3.1	3.8	70.2	9.8	20.0	29.8
72	14.2	76.2	2.6	5.1	70.9	9.7	19.4	29.1
74	0	69.3	2.9	5.4	68.9	8.1	23.0	31.1

Sample: Hiawatha Coal

Size: -100 mesh

Catalyst: none

Temperature: 450°C

Pressure: 2000 psi

Coal dried 18 hours at 110° with 0.5% starch added

Feed Rate: 5 g/min.

APPENDIX A

TABLE VII

SOLIDS-PRODUCT DISTRIBUTION WITH TIME OF DRYING

Figure 8

Test Number	Hours at 110°C	Solids Distribution Percent			Product Distribution, Percent			
		Wet	Dry	Between	Solids	Liquids	Gases	Conversion
81	18	17.5	35.6	---	45.6	14.8	39.6	54.4
82	68	50.3	10.7	4.7	60.4	13.7	25.9	39.6
77	114	67.6	2.4	4.9	68.3	10.1	21.6	31.7

Sample: Hiawatha

Size: -100 mesh

Catalyst: None

Temperature: 475°C

Pressure: 2000 psi.

Coal agglomerated with 0.5% starch

Feed Rate: 5 g/min.

APPENDIX A

TABLE VIII

SOLIDS-PRODUCT DISTRIBUTION, TEMPERATURE OF DRYING

Figure 9

Test Number	Temp. of Drying	Solids Distribution Percent			Product Distribution, Percent			
		Wet	Dry	Between	Solids	Liquids	Gases	Conversion
81	110	17.5	35.6	---	45.6	14.8	39.6	54.4
86	128	66.6	3.3	4.6	65.9	12.7	21.4	34.1
91	132	69.4	3.6	3.4	66.9	14.6	18.5	33.1
85	145	73.1	1.7	4.2	77.4	4.3	18.3	22.6
84	184	72.4	1.5	5.7	79.6	3.8	16.6	20.4

Sample: Hiawatha

Size: -100 mesh

Catalyst: None

Temperature: 475°C

Pressure: 2000 psi.

Coal agglomerated with 0.5% Starch

Dried for 18 hours

Feed Rate: 5 g/min.

APPENDIX A

TABLE IX

SOLIDS-PRODUCT DISTRIBUTION, HOURS OF DRYING AT 128°C

Figure 10

Test Number	Hours of Drying	Solids Distribution Percent			Product Distribution, Percent			
		Wet	Dry	Between	Solids	Liquids	Gases	Conversion
91	18	69.4	3.6	3.4	66.9	14.6	18.6	33.1
86	20	66.6	3.3	4.6	65.9	12.7	21.4	34.1
88	48	69.1	2.4	5.9	65.9	15.5	18.6	34.1
87	70	65.5	2.1	3.8	64.4	10.7	24.9	35.6

Sample: Hiawatha

Size: -100 mesh

Catalyst: None

Temperature: 475°C

Pressure: 2000 psi.

Coal agglomerated with 0.5% starch

Dried at 128°C

Feed Rate: 5 g/min.

APPENDIX A

TABLE X

SAMPLE FEED RATE

Figure 11

Test Number	Feed Rate g/m	Solids Distribution Percent			Product Distribution, Percent			
		Wet	Dry	Between	Solids	Liquids	Gases	Conversion
126	5	52.8	8.3	8.2	29.2	56.4	14.4	70.8
130	20	40.3	19.0	2.9	34.1	34.1	31.8	65.9
128	35	48.0	13.8	2.4	32.2	36.0	31.8	67.8
129	50	54.6	15.5	4.2	40.5	39.6	19.9	59.5

Sample: Hiawatha

Size: -100 mesh

Catalyst: $SnO_2 \cdot 2H_2O$ Sn/Coal Ratio 0.09-0.11

Temperature: 557°C

Pressure: 2000 psi.

Coal agglomerated with 0.59% starch

Dried 18-20 hours at 128°C

APPENDIX A

TABLE XI

SOLIDS AND PRODUCT DISTRIBUTION WITH VARYING CONCENTRATION OF CATALYST

Figure 12

Test Number	Sn/Coal Ratio	Solid Distribution Percent			Product Distribution, Percent			
		Wet	Dry	Between	Solids	Liquids	Gases	Conversion
143	0.231	55.5	8.4	7.6	19.5	64.0	16.5	80.5
144	0.169	62.0	8.2	3.8	28.8	56.1	15.1	71.2
145	0.0639	40.7	12.7	6.2	23.9	47.0	29.1	76.1
146	0.118	51.3	14.2	1.9	19.1	50.8	30.1	80.9
147	0.0184	55.4	7.8	5.2	50.6	27.4	22.0	49.4

Sample: Hiawatha

Size: -100 mesh

Catalyst: $SnCl_2 \cdot 2H_2O$ Varying

Temperature: 578°C

Pressure: 2000 psi.

Coal agglomerated with 0.57% starch

Dried 18-20 hours at 128°C

Feed Rate: 5 g/min.

APPENDIX A

TABLE XII

SOLIDS AND PRODUCT DISTRIBUTION

ASSAM, INDIA COAL

Figure 13

Test Number	Temp. °C	Solids Distribution Percent			Product Distribution, Percent			
		Wet	Dry	Between	Solids	Liquids	Gases	Conversion
155	578	44.6	20.1	7.8	29.0	53.1	16.9	70.0
156	640	36.9	19.9	4.5	28.9	41.1	30.0	71.1
157	517	55.4	7.8	7.3	35.0	41.3	23.7	65.0

Sample: Assam, India Coal

Size: -100 mesh

Catalyst: $SnCl_2 \cdot 2H_2O$ Sn/Coal Ratio = 0.10

Pressure: 2000 psi.

Coal agglomerated with 0.5% starch

Dried 18-20 hours at 128°C

Feed Rate: 5 g/min.

APPENDIX A

TABLE XIII

SOLIDS AND PRODUCT DISTRIBUTION

COALVILLE, UTAH COAL

Figure 14

Test Number	Temp. °C	Solids Distribution Percent			Product Distribution, Percent			
		Wet	Dry	Between	Solids	Liquids	Gases	Conversion
122	557	54.6	7.6	9.1	36.2	49.7	14.0	63.8
123	600	51.9	9.1	6.0	28.2	52.5	19.3	71.8
124	516	56.6	6.4	7.2	40.1	45.9	14.0	59.9
125	475	54.7	6.5	7.8	45.4	38.2	16.4	54.6
135	578	49.2	11.3	2.8	26.8	46.2	27.0	73.2
136	599	54.4	8.9	4.1	33.7	45.9	20.4	66.3
137	557	55.9	8.1	4.4	32.7	48.6	18.7	67.3

Sample: Coalville, Utah Coal

Size: -100 mesh

Catalyst: $SnCl_2 \cdot 2H_2O$ Sn/Coal Ratio = 0.10

Coal agglomerated with 0.5% starch

Dried 18-20 hours at 128°C

Feed Rate: 5 g/min.

APPENDIX A

TABLE XIV

SOLIDS AND PRODUCT DISTRIBUTION

HIAWATHA, UTAH COAL

Figure 15

Test Number	Temp. °C	Solids Distribution Percent			Product Distribution, Percent			
		Wet	Dry	Between	Solids	Liquids	Gases	Conversion
118	557	46.3	9.7	11.5	27.9	52.4	19.7	72.1
119	600	40.6	9.5	9.2	26.1	47.6	26.2	73.8
120	516	59.3	4.4	8.3	45.1	36.7	18.2	54.9
121	475	65.1	3.4	7.9	48.1	33.1	18.7	51.8
134	578	47.5	11.1	7.6	28.8	49.0	22.2	71.2
138	599	33.9	7.4	9.8	26.5	42.1	31.4	73.5
139	640	33.7	18.8	6.1	24.7	45.4	29.9	75.3
164	578	50.5	9.0	11.8	26.9	53.6	19.5	73.1
133	557	45.2	9.8	7.3	34.3	42.8	22.1	65.7

Sample: Hiawatha, Utah Coal

Size: -100 mesh

Catalyst: $SnCl_2 \cdot 2H_2O$ Sn/Coal Ratio: 0.10

Coal agglomerated with 0.5% starch

Dried 18-20 hours at 128°C

Feed Rate: 5 g/min.

APPENDIX A

TABLE XV

AVERAGE VALUES OF PRODUCTS FOR ASSAM, COALVILLE AND HIAWATHA COALS

Figure 16

	Product Distribution, Percent, Average			
	Solids	Liquids	Gases	Conversion
Assam	31.3	45.2	23.5	68.7
Coalville	34.7	46.7	18.6	65.3
Hiawatha	32.1	44.7	23.2	67.9

APPENDIX A

TABLE XVI

SOLIDS AND PRODUCT DISTRIBUTION, COALVILLE COAL, $ZnCl_2$ CATALYST

Figure 17

Test Number	Zn/Coal Ratio	Solids Distribution Percent			Product Distribution, Percent			
		Wet	Dry	Between	Solids	Liquids	Gases	Conversion
159	0.0754	50.4	19.5	10.1	23.3	52.6	24.1	76.6
161	0.0321	55.7	14.3	7.7	29.9	45.4	24.7	76.1
163	0.0926	59.8	12.0	7.2	25.7	48.6	25.7	74.3
169	0.0603	54.2	18.8	5.4	23.4	51.9	24.7	76.6
170	0.0811	62.6	10.4	7.4	23.1	53.5	23.4	76.9
171	0.0412	65.0	9.4	9.0	32.9	49.1	18.0	67.1
172	0.0509	69.9	6.9	10.7	28.6	57.1	14.3	71.4
176	0.0196	68.8	7.6	8.3	42.8	41.0	16.2	57.2

Sample: Coalville Coal

Size: -40 mesh

Catalyst: $ZnCl_2$

Coal agglomerated with 0.5% Starch

Dried 18-20 hours at 128°C

Feed Rate: 5 g/min.

Temperature: 578°C

Pressure: 2000 psi.

APPENDIX A

TABLE XVII

SOLIDS AND PRODUCT DISTRIBUTION, COALVILLE COAL, PARTICLE SIZE

Figure 18

Test Number	Particle Size	Solids Distribution Percent			Product Distribution, Percent			
		Wet	Dry	Between	Solids	Liquids	Gases	Conversion
149	-100	58.0	9.4	7.5	24.5	46.1	29.4	75.5
159	- 40	50.4	19.5	10.1	23.3	52.6	24.1	76.6
165	- 20	46.1	19.5	7.2	20.7	46.9	32.4	79.3
166	- 60	60.1	12.6	11.0	24.9	56.0	19.1	75.1
167	- 80	59.7	13.7	10.1	21.8	59.0	19.2	78.2
174	- 10	52.3	20.7	5.4	27.1	47.6	25.3	72.9

Sample: Coalville Coal

Catalyst: $ZnCl_2$

Coal agglomerated with 0.5% Starch

Dried 18-20 hours at 128°C

Feed Rate: 5 g/min.

Temperature: 578°C

Pressure: 2000 psi.

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Projects IV(b) and V(a). SOLVENT EXTRACTION OF COAL BY ORGANIC SOLVENTS AND THE EFFECTS OF ULTRASONIC ENERGY ON EXTRACTION

Work on dissolution of coal and solvent extraction of coal at temperatures above the solvent boiling temperatures have been covered in other parts of this report.

The results of extraction indicated that only limited parts of the coal was soluble at lower than boiling temperatures and that more expensive equipment was required for extraction at higher temperatures since higher pressures had to be maintained.

Research on solvent extraction at temperatures from 24°C to 87°C was done to see if higher yields of product could be obtained without pressures higher than atmospheric.

Coal was extracted with hydrogen-donor solvents, especially tetralin, and other solvents in ordinary ultrasonic cleaners. Experiments were conducted with and without ultrasonic energy being present. The effects of ultrasonic energy were observed both on the yield of extract and in the rate of extraction for high volatile bituminous coal.

Materials and Procedure

Coal used for the experiments was Spring Canyon Coal, a high volatile bituminous coal of 45.7% volatile matter and 45.9% fixed carbon. The experiments were conducted in two different ultrasonic cleaners, both having energy inputs of 0.59 watts per square centimeter of tank area. One apparatus had a control for varying the amount of total energy which was made available to the cleaning tank (reaction vessel). Solvents used were practical or analytical grade chemicals. Some experiments were done with coal and solvent in glass containers. It was found that the glass filtered out some of the ultrasonic energy. Experiments had to be done to find the coal: solvent ratios which could be used without saturating the solvent with extract, thus artificially limiting the reaction.

The experiments were conducted by using ground coal mixed with solvent. This was placed in the ultrasonic tank at the reaction temperature. After the desired time the coal-solvent was removed and washed with a poor coal solvent such as acetone to remove the solvent and extract. The per cent of extract was determined by the amount of undissolved coal remaining after reaction.

Results and Conclusions

Results for experiments at 24°, 34° and 54° for coal extraction with tetralin show the effect on yield of ultrasonic energy. This data is shown in Table I. Results at higher temperatures showed similar increases when ultrasonic energy was employed. Following are data at 97°C, the highest temperature used:

Solvent	Fraction Extracted %
Tetralin	21.2
Ethylenediamine	28.5
Pyridine	35.6
Methyl cyclohexane	13.1
Carbon Disulfide	15.3
Dichloromethane	12.1

Extraction time: 9 hours
Power input: 3.75 watts/in^2

The effectiveness of ultrasonic energy to make the coal available for solution by a solvent is especially evident in the cases where completely ineffective solvents were used. For example, methylcyclohexane does not dissolve coal to any measurable amount at temperatures up to 100°C. However, in the presence of ultrasonic energy 13.1% was extracted. The reasons for this remarkable difference is not completely understood but kinetic data help to show the kind of energies involved in the reactions.

Kinetic data were obtained for tetralin extraction of coal. The results indicate that the rate of and ability of the extract to dissolve the coal in the presence of ultrasonic energy is accelerated due to dispersal of the coal micelles but without decomposition of large extractable molecules. The value of 6.0 kilocalories per mole for activation

enthalpy indicates that only van der Waals forces, or hydrogen bonding (2-8 kcal/mole), are probably involved in the breaking of the coal during extraction.

TABLE I

YIELDS OF EXTRACT AFTER 20 HOURS IN THE PRESENCE AND ABSENCE OF ULTRASONIC ENERGY

Extraction Temp. (°C)	Yield (wt.%)	
	Without Ultrasonic Effect	With Ultrasonic Effect
24	3.70	10.21
34	3.97	10.61
54	4.10	11.41

Projects V and V(b). SOLVENT EXTRACTION OF COAL BY SOLVENTS

Introduction

As known reserves of naturally occurring liquid and gaseous fuels are becoming more limited in quantity, and as the cost of locating and exploiting new reserves increases, the production of liquid and gaseous fuels from coal on an economic and competitive basis appears to be imminent in areas of low cost coal. Such economic conversion processes depend upon an understanding of the basic physical and chemical nature of coal, as well as an understanding of the rates and mechanisms of the reactions which may yield liquid and gaseous products with the desired properties. Kinetic studies of the processes involving the dissolving of coal in solvents have been conducted in this laboratory[1,2]. Presented here is an analysis of typical data thus obtained leading to a proposed mechanism of the solution process.

Experimental Procedure

The high volatile bituminous coal used in this study was taken from Spring Canyon Mine in Utah, with volatile matter content of 45.7%, and consisting of 72.9% Carbon and 5.6% hydrogen. The coal was crushed and sized to pass 200 mesh. The solvent used was technical grade tetralin. The equipment consisted of a one-liter autoclave equipped with a magnedrive

stirring device, a water quenching system, external heater, pressure gauge and liquid and gas sampling lines. Also included were a temperature controller, potentiometer and relays.

The experimental procedure utilized is as follows:

Approximately 450 ml of tetralin were placed in the reactor, which was then evacuated to remove the air. The reactor was filled with helium to a slight positive pressure and brought to the desired temperature. With the stirrer operating at 1500 rpm, the coal paste, consisting of 50 gms. of coal well mixed in 50 ml of tetralin, was injected into the tetralin in the reactor. The injection operation required approximately two minutes, and produced a temperature decrease of about 8°C. The temperature rapidly returned to the predetermined reaction temperature, where it was maintained within $\pm$ 3°C.

Small liquid samples (ca. 20 ml) were periodically obtained through the water-cooled sampling lines and each sample was placed in a weighed double-thickness Soxhlet extraction thimble. The sample was then extracted with benzene, and the quantity of benzene-soluble components determined gravimetrically. Reproducibility of the data was determined to be within $\pm$ 5 percent.

Gas samples were also obtained and analyzed by gas chromatography and by mass spectrometry.

A ratio of 10 ml of solvent per gram of coal was used in all of the experiments reported here.

Results and Discussion

Typical time-yield curves from this study are shown in Figure 1. Constant temperature data were obtained at eight temperatures ranging between 350° and 450°C.

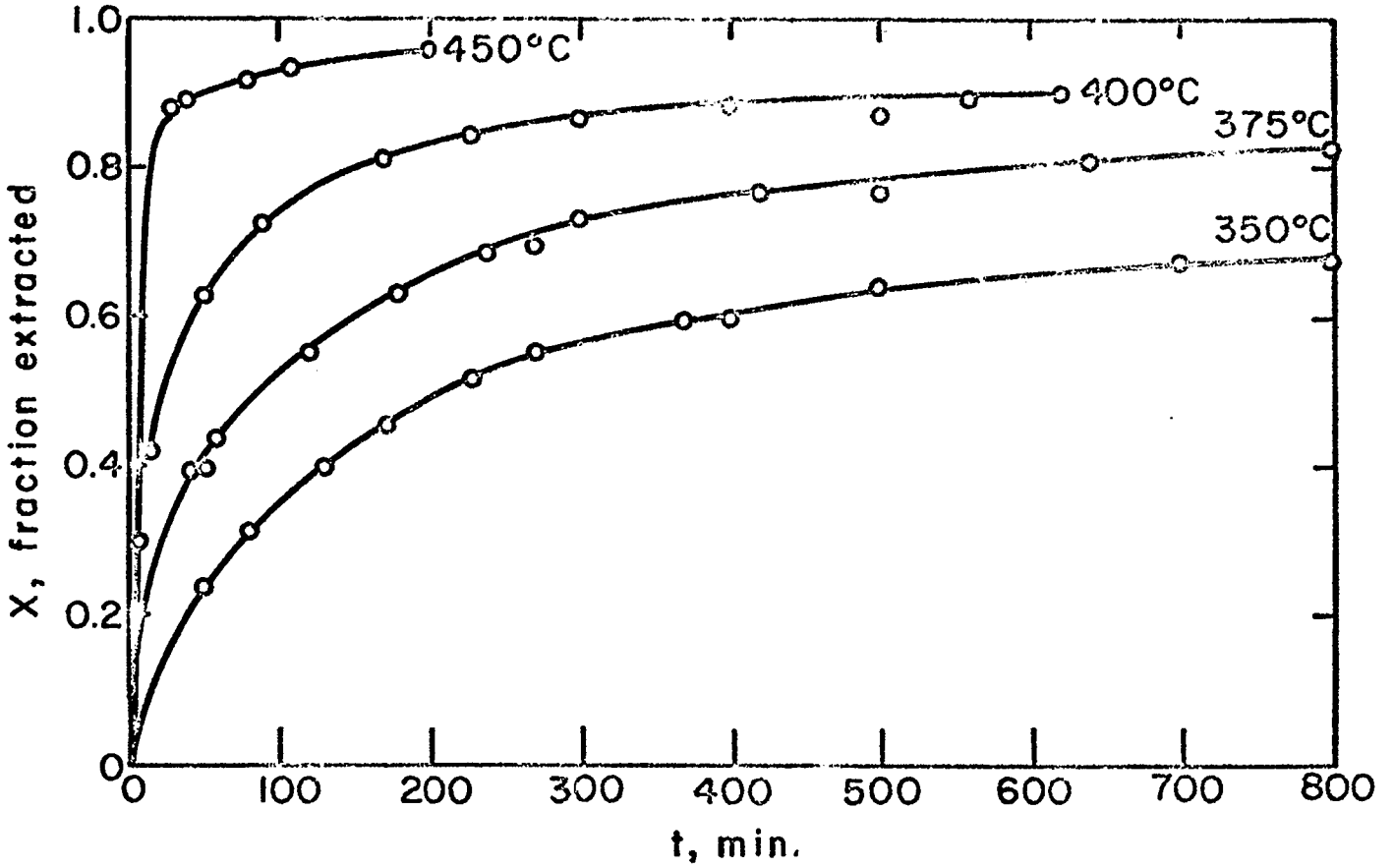
To analyze the data kinetically, a second order differential equation is written:

$$\frac{dx}{dt} = k_2 (a-x) (b-x) \qquad (1)$$

where "x" is the amount of coal extracted in time "t", as a fraction of the initial sample weight, "a" is the maximum weight fraction of coal extracted at the temperature under consideration, and "b" is the weight fraction of tetralin (assumed equal to 1.0) which could potentially react. The constant "k_2" is the reaction velocity constant. Integrating equation (1) and evaluating the constant of integration with x=0 when t=0 yields:

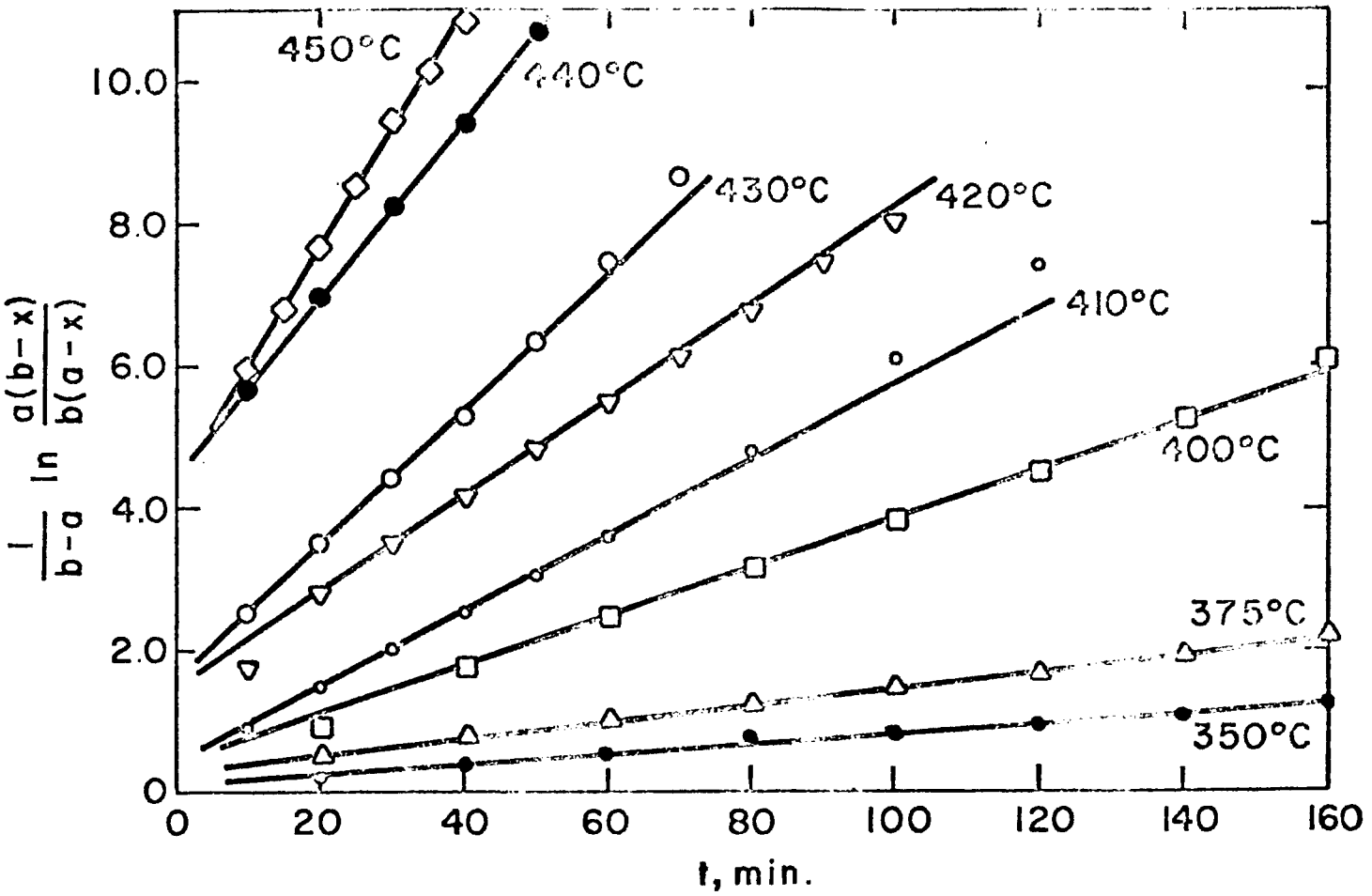
$$\frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} = k_2 t \qquad (2)$$

Figure 2 is a plot of the second order rate equation. It is noted that the data produce straight lines, and hence are second order, throughout



TIME-YIELD CURVES

Fig. 1



PLOT OF SECOND ORDER EQUATION

Fig. 2

most of the reaction at all temperatures considered, the fraction of total product yield under second order conditions ranging from 63% at 350°C to 94% at 450°C.

Figure 3 is a plot of a first order rate equation. It is noted that the data approximate straight lines, and hence appear first order, only in the latter portions of the determinations at each temperature.

A region of transition is observed between the second order and first order regions of the data.

The rate of a chemical reaction is determined by the free energy of activation, $\Delta F^{\ddagger}$. Following the procedure presented in the Absolute Reaction Rate Theory of Eyring and realizing that the number and nature of reaction sites in a heterogeneous system, such as solution of coal in a solvent, changes with time, as discussed by Hill, we can write:

$$k' = \frac{\text{Molar conc. of sites}}{\text{gram}} \quad \frac{\kappa k t}{h} \; e^{-\Delta H^{\ddagger}/RT} \; e^{\Delta S^{\ddagger}/R} \qquad (3)$$

which may be written in the form:

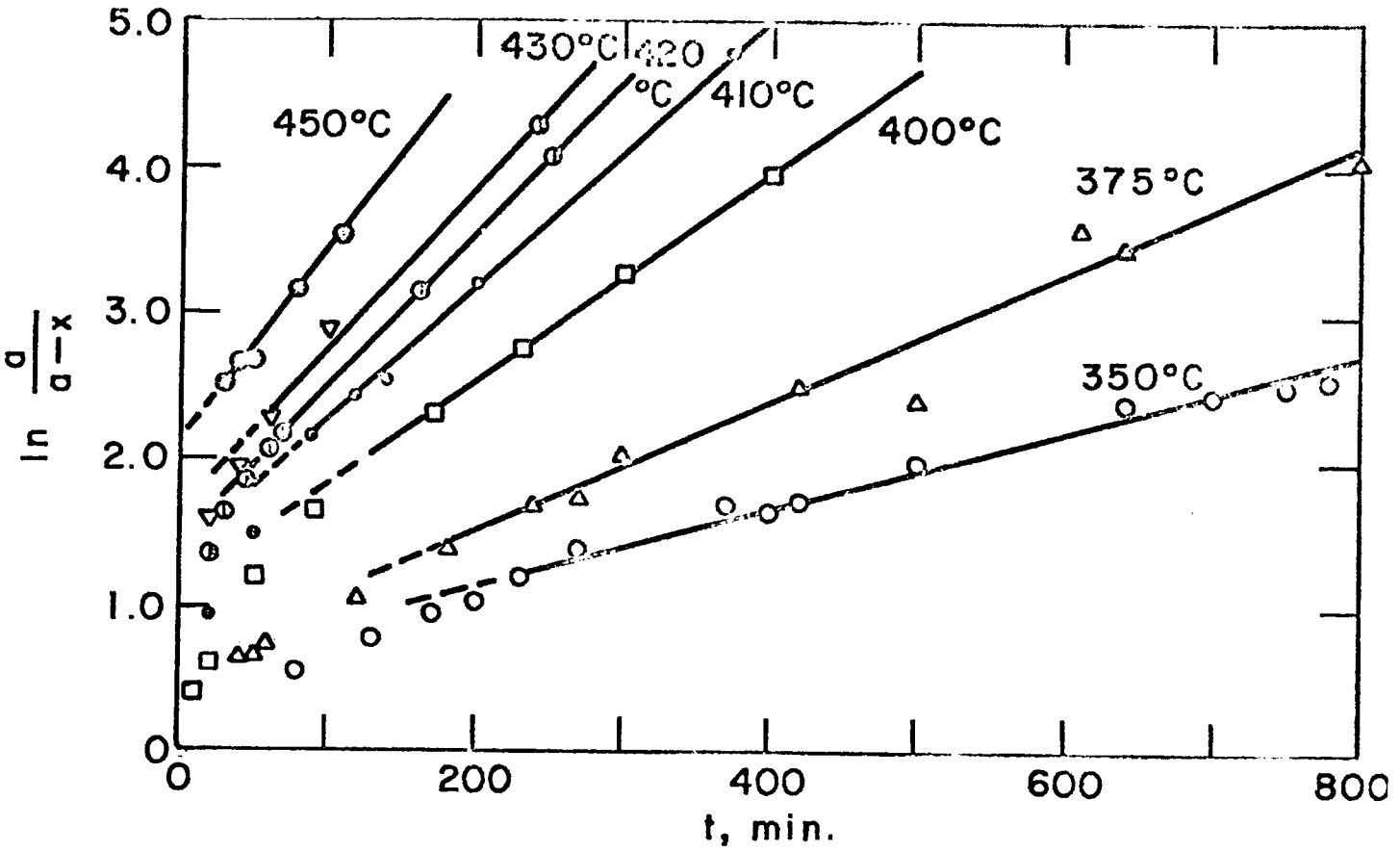
$$\ln \left(\frac{h}{\kappa k} \quad \frac{k'}{T}\right) = - \frac{\Delta H^{\ddagger}}{R} \; \frac{1}{T} + \frac{\Delta S^{\ddagger}}{R} + \ln \alpha \qquad (4)$$

where α denotes the molar concentration of active sites per gram of coal. The transmission coefficient, κ, is taken as unity.

From equation (4) a plot of $\ln \left(\frac{h}{\kappa k} \quad \frac{k'}{T}\right)$ vs $\frac{1}{T}$ will yield a straight line with slope equal $\frac{-\Delta H^{\ddagger}}{R}$ and intercept equal to $\left(\frac{\Delta S^{\ddagger}}{R} + \ln \alpha\right)$. Figure 4 presents such a plot of the data for the second order region. This plot yields a value for $\Delta H^{\ddagger}$ of 28.8 kcal per mole. The intercept at $\frac{1}{T} = 0$ yields a value for $(\Delta S^{\ddagger} + R \ln \alpha)$ of -14.8 units. A similar plot for the first order region yields values of 15.6 kcal. per mole for $\Delta H^{\ddagger}$ and -37.7 units for $(\Delta S^{\ddagger} + R \ln \alpha)$ for that region.

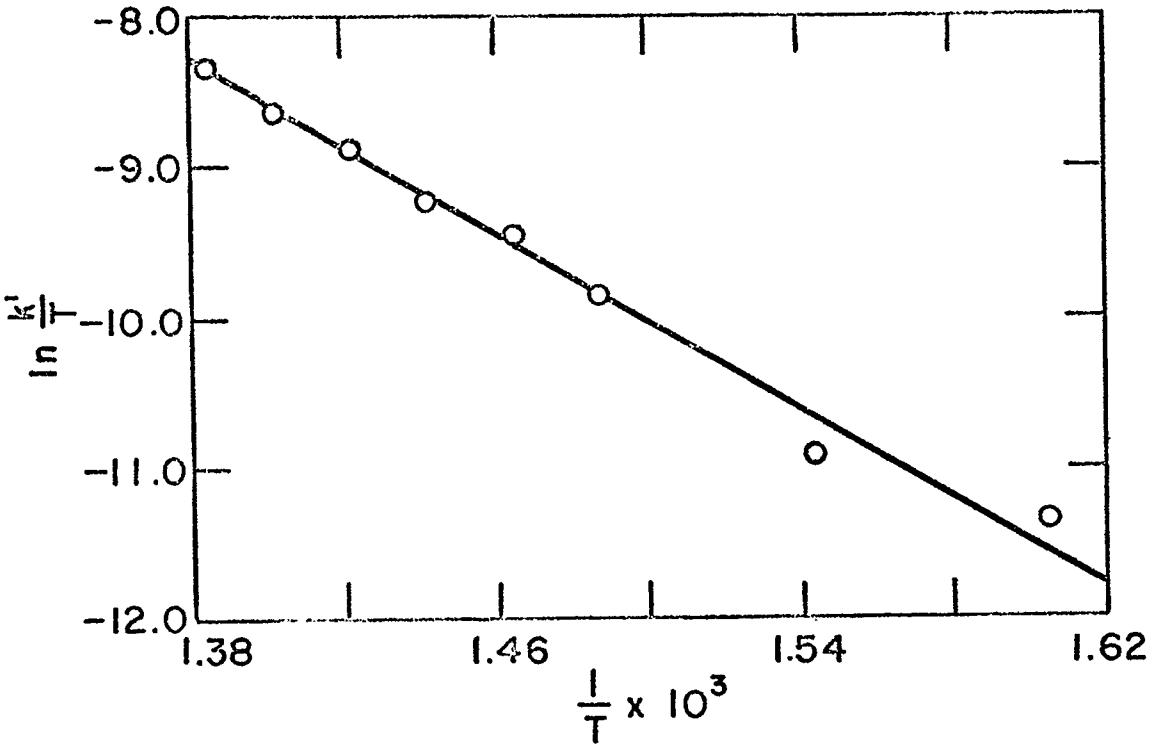
It has been noted that in the temperature range under consideration in this study most of the product yield occurs under reaction conditions involving second order reactions. Inasmuch as coal is an extremely complex substance, there are undoubtedly many reactions which contribute to the product yield. The data indicate that the rate of product yield is controlled by reactions which are second order, i.e. the rate of product yield is proportional to the concentration (or more precisely the activity) of each of two reactants or to the square of the concentration (or activity) of one reactant. (Other possibilities also exist.) The magnitude of the enthalpy of activation of 28.8 kcal per mole indicates that chemical reactions and not physical processes are rate controlling.

Examination of the data (e.g. Figure 1) reveals that the rate of product yield decreases as the amount of unreacted coal decreases, and that this relationship continues throughout the extraction process. It



Plot of first order equation.

Fig. 3



Absolute reaction rate plot for evaluating $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, second order region.

Fig. 4

may thus be concluded that the rate is dependent upon the concentration of unreacted coal which may potentially react under the conditions of the particular experiment.

Preliminary studies were conducted to determine the effect of solvent concentration upon reaction velocity. The results of these studies are given in Figure 5. It is observed that for a given time and constant temperature (6 hours at 400°C) the amount extracted continued to increase with increasing solvent/coal ratio to a value of 8 cc. of solvent per gram of coal, or assuming a coal density of 1.35 g/cc.[13], a volume ratio of 11 cc. of tetralin per cc. of coal, a very large excess of solvent. With the thorough agitation maintained in the system throughout the reaction time, quantities of solvent greater than this could ensure essentially pure solvent (solvent mole fraction of approximately 1.0 at the external surface of the coal particles throughout the reaction time of 6 hours.

Considering the large extent of the internal surface area of the coal compared with the external area of the coal particles, it is apparent that most of the reaction between coal and solvent occurs within the coal. Although the stirring operation may ensure a fresh supply of solvent at the external surface of the coal particle, it cannot accomplish this within the pores of the coal. In order for reaction between coal and solvent to proceed within the pores, solvent must diffuse into the pore to the potential reaction site. Similarly, products must diffuse from the internal areas out of the pores.

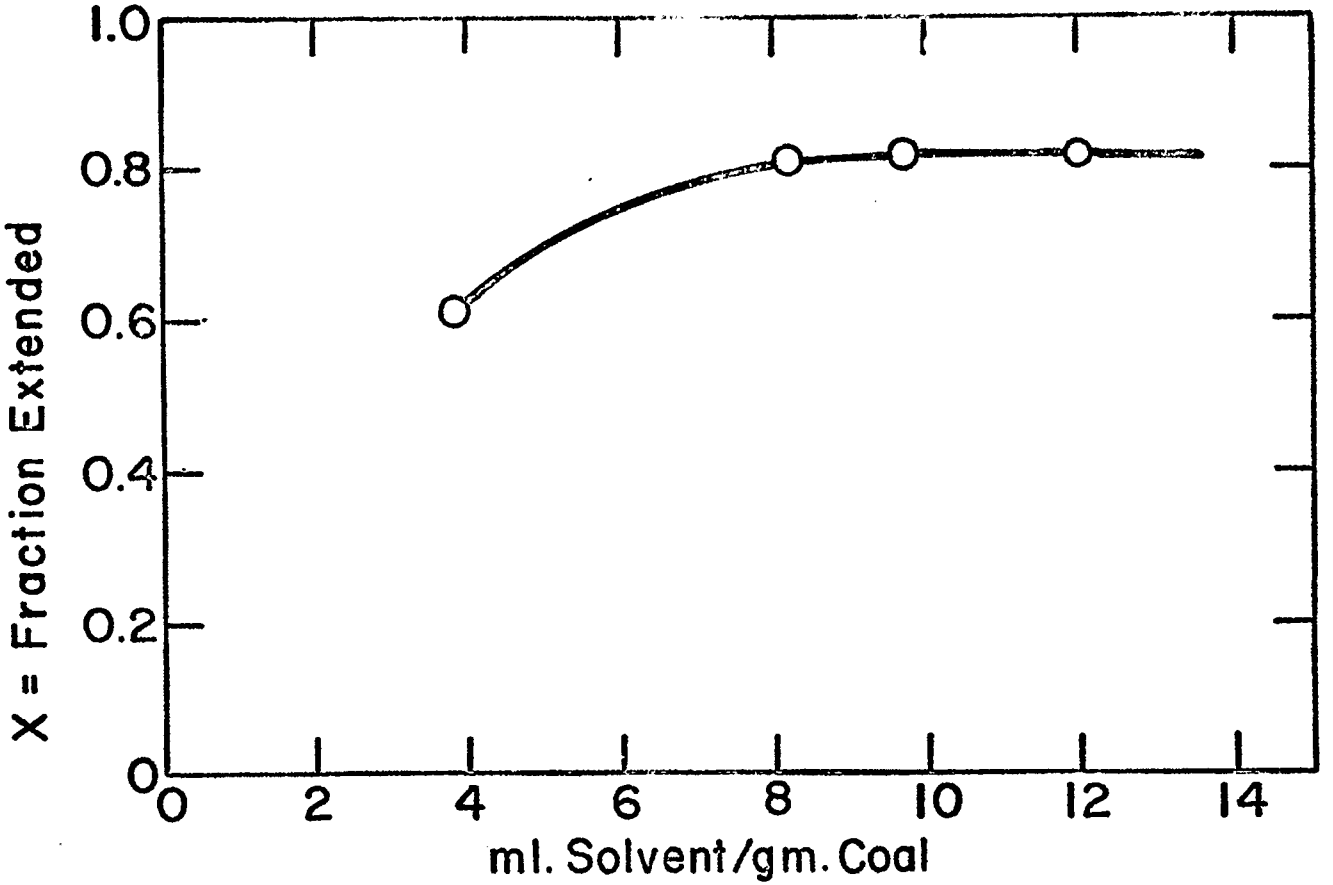
According to Fick's law of diffusion through liquids the quantity of material diffusing per unit time is proportional to the area and to the concentration gradient in the direction of diffusion. Expressed mathematically:

$$\frac{dN}{dt} = - DA \frac{dC}{dZ} \qquad (5)$$

where N = No. of moles of substance transferred
t = time, sec.
D = diffusion coefficient, cm^2/sec.
A = area, sq. cm.
C = concentration, moles/cc (concentration is proportional to mole fraction)
Z = distance measured in the direction of diffusive flow, cm.

According to this expression, the concentration gradient would be greatest, and the reaction rate maximum, when the mole fraction of solvent is 1.0 and the mole fraction of reaction product zero at the pore exit. The data of Figure 5 indicate the large quantity of solvent required to essentially maintain this condition with thorough agitation. (Actually the mole fraction of product at the pore exit is not zero, but a low value such that it is not reflected by the experimental techniques of the present study.)

Figure 5 yields a qualitative picture of the dependence of the dissolution rate upon mole fraction or concentration of solvent. For a fixed



Effect of solvent/coal ratio upon reaction at 400°C and 6 hours.

Fig. 5

time of six hours at constant temperature, the extent of product yield increases as the quantity of solvent in the system increases, reaching a maximum when sufficient solvent is present to effectively maintain a solvent mole fraction in the liquid of approximately 1.0 at the pore exit of the coal particles. This means that the extent of product yield per unit time increases as the concentration gradient between pore exit and reaction site increases [equation (5)] or as the quantity of solvent supplied to the reaction site increases. It is therefore concluded that the dissolution rate is dependent upon the concentration of unreacted solvent at the reaction site.

In equation (1) the term (a-x) denotes a first order dependence of the dissolution rate upon the concentration of unreacted coal, with the quantity "a" denoting the maximum quantity of coal available for reaction at the temperature concerned. The term (b-x) denotes a first order dependence of rate upon the concentration of solvent, all of the solvent being potentially available for reaction.

The gaseous products of the reactions were analyzed at each temperature with the aid of a F & M Model 720 gas chromatograph and a Consolidated Electrodynamics Model 21-620 mass spectrometer. The principal components of the gases were hydrogen, methane, ethane and traces of propane and hydrogen sulfide. Figure 6 shows the percentages of each component at the various temperatures. As the temperature of extraction is increased, the following trends are observed:

(1) The percentage of hydrogen in the gas decreases, slowly at the lower temperatures but rapidly above 410°C.

(2) The percentage of methane in the gas increases rather steadily, from about 5% at 350°C to 28% at 430°C.

(3) The percentage of ethane increases rather steadily, but with considerably smaller amounts than the methane.

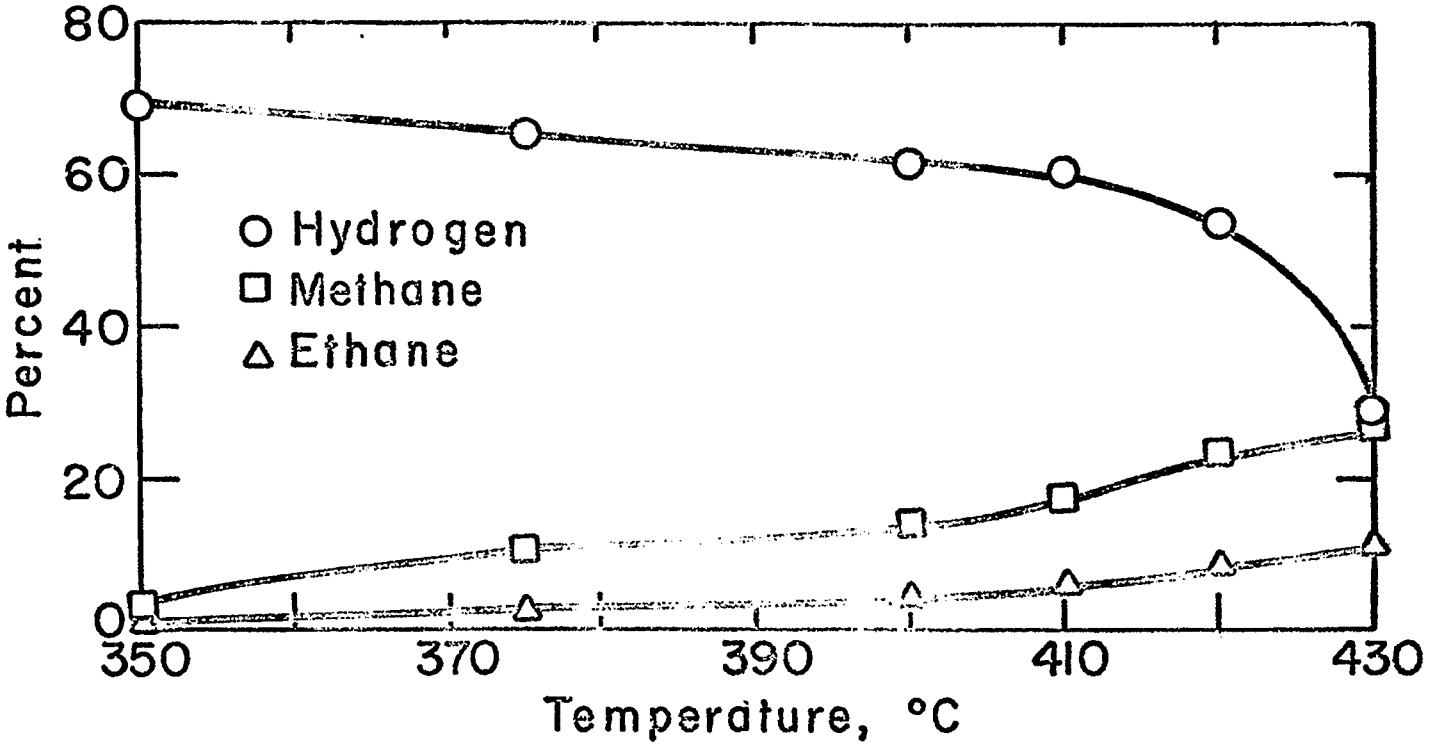
The decomposition of tetralin in the absence of coal, as indicated by the production of hydrogen in the gas and naphthalene and its homologs in the liquid, was negligible below about 425°C. The decomposition then increased somewhat, but was less than 10% at 450°C.

An analysis of the liquid products produced by the reaction of tetralin with coal showed the following trends as the temperature of extraction increased:

(1) The decomposition of tetralin increased steadily, becoming extensive above 400°C.

(2) The quantity of naphthalene in the liquid products increased.

(3) The quantities of low boiling constituents in the liquid increased, as indicated by a decrease in the initial boiling point of the liquid, and by an increase in the quantity distilled below the boiling point of



Chromatographic analysis of gaseous products of solvent extraction.

Fig. 6

tetralin. These results are shown in Figure 7. As the quantity of naphthalene in the vapors became appreciable, the condensing naphthalene formed crystals and plugged the condenser, thus terminating the distillation experiment.

The following qualitative observations were made[4]:

(1) At a given temperature, the production of naphthalene is much greater in the coal-tetralin system than when tetralin is heated alone.

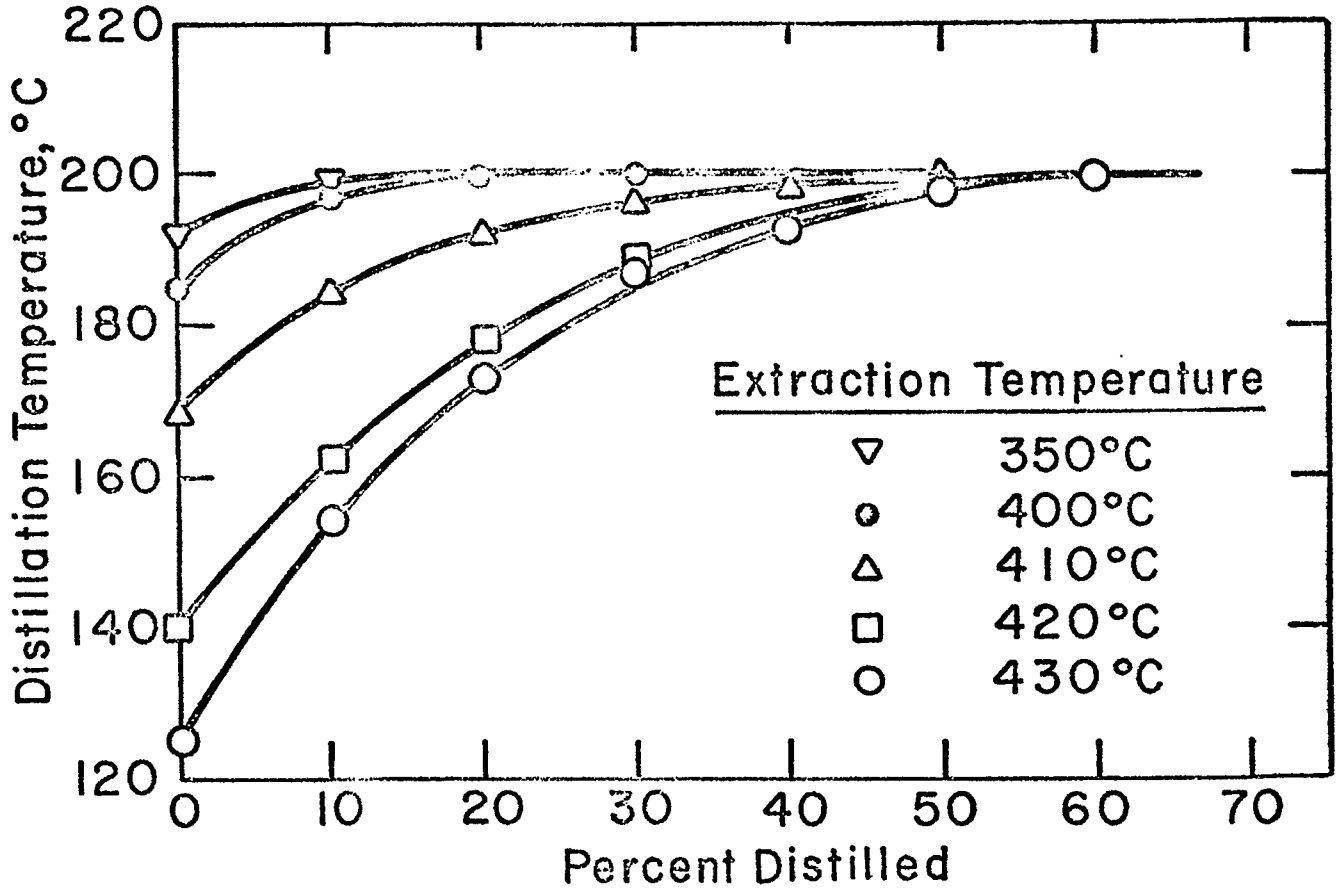
(2) At a given temperature, the production of hydrogen is greater in the coal-tetralin system than the sum of the productions when each is heated separately in this temperature range.

The above analytical observations lead to certain conclusions concerning the mechanism of the dissolution of bituminous coal in tetralin at temperatures ranging from 350° to 450°C.

Thermal decomposition of bituminous coal becomes appreciable above 350°C, as indicated by the appearance of the plastic state in this temperature range. This decomposition involves the rupture of linkages joining adjacent aromatic clusters. These ruptures produce free radicals which if stabilized, and if small enough, may appear as extract in the solvent. Stabilization may conceivably occur by a rearrangement of atoms within the fragment, by the addition of atoms or groups of atoms to the fragment, or by the polymerization of the fragments.

Superimposed upon the thermal decomposition reactions are reactions involving the solvent, tetralin. The rather extensive appearance of naphthalene in the liquid extraction products, as compared with the small amounts of naphthalene and its homologs produced from pure tetralin at the same temperature, indicates an appreciable reaction between the coal and the tetralin. Such reactions if occurring on the surface, external or internal, of the coal, would possibly proceed at the conditions of reduced activation energy characteristic of surface catalysis reactions. These interactions between coal and tetralin would likely result in much more extensive rupture of connecting bridges between aromatic clusters than would be observed in the absence of the solvent at the same temperature.

The production of naphthalene from tetralin involves the release of hydrogen atoms which, being thus released in the immediate vicinity of the thermally ruptured bonds, provide a means of stabilization of the coal fragments. These stabilization reactions would yield product "molecules" characteristic of the parent coal. Bituminous coal is understood to consist essentially of fused aromatic clusters, with from one to several rings per cluster, an average being about four. Lesser amounts of hydroaromatic clusters would, after stabilization of the aliphatic fragment by hydrogen atoms from the tetralin, yield methane, ethane, and small amounts of propane or higher homologs. The extent of these reactions, and the corresponding yields of methane and ethane, would increase as the extraction temperature increases. Yields of these compounds as determined in this study are in harmony with such a model.



Distillation of liquid products of extraction.

Fig. 7

Stabilization of the aromatic fragments would yield "molecules" ranging in size from benzene to particles containing many fused aromatic rings. As the temperature increases, the rupture of connecting bridges would become more extensive, thus yielding fewer very large fragments and in the limit approaching an average size of about four aromatic rings per "molecule". Such a particle would have a minimum molecular weight of 202. Evidence is lacking which would indicate appreciable rupture of carbon-carbon bonds within the fused aromatic clusters at these temperatures. Experimental determinations of the molecular weights of the particles in solution, as produced in solvent extraction of bituminous coal at elevated temperatures, demonstrate the presence of a major proportion in the range of molecular weights of 300 to 1000. Allowing for incomplete rupture of connecting bridges, together with attached hydroaromatic or aliphatic segments, these observations support the model proposed herein.

Considering the high degree of unsaturation of the aromatic clusters, as indicated by the carbon-hydrogen ratio in coal, the opportunities for stabilization of these clusters through rearrangement of the atoms would be few. The presence of atomic hydrogen as released from the tetralin would tend to inhibit the polymerization of adjacent aromatic free radicals, especially at the higher temperatures of this study. Consequently the greater portion of the stabilization process would be accomplished by the addition of hydrogen atoms to the free radicals.

It was observed that the rate of product yield assumed first order characteristics in the later portions of the dissolution process. It would be expected that as the reactions at the surfaces within the coal structure proceed, the pores are enlarged, as well as the channels through which the tetralin must diffuse. Thus, while the reaction rate is diminishing due to the decrease in quantity of unreacted coal [equation (1)], it becomes increasingly easy to supply fresh tetralin to the reaction site. Ultimately a time is reached when an excess of solvent is present at the reaction sites, as reflected in the experimental procedure, at which time the reaction velocity is no longer dependent upon the concentration of the solvent. The reaction is then first order with respect to unreacted coal only. A gradual decay from second order to first order was noted, as would be expected with this model.

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Project V(c). KINETICS OF HYDROGENATION OF PURE POLYNUCLEAR HYDROCARBONS

Introduction

As one attempts to convert coal to useful liquid materials, it seems desirable to obtain high yields of benzene and its derivatives. These compounds have wide applicability as additives in gasoline to improve the octane rating as raw materials for the manufacture of conventional explosives, as solvents and chemicals, etc. The higher members of the aromatic homologous series are solids at room temperature. (The melting point of naphthalene, a two-ring structure, is 80°C.)

In the course of coal pyrolysis, a single-ring aromatic constituent existing in the lattice structure may possibly be liberated by rupture of the bond(s) joining it to the structure, followed by stabilization of the fragment thus produced. Similarly, higher members of the aromatic homologous fused series may be produced. These products may then be liberated as volatile products as determined by their respective vapor pressures.

These processes are greatly assisted by the presence of an agent which can produce atoms or small radicals to stabilize the thermally-produced fragments. Hence, dissolution in an appropriate solvent (e.g., tetralin) produces larger quantities of lower-boiling aromatic materials. Hydrogenation in the presence of an appropriate catalyst yields yet larger quantities of lower-boiling constituents.

The production of benzene and its derivatives may be increased by hydrogenation and hydrocracking of higher members of the aromatic series. For members of the series consisting of three rings or more, two possible approaches may exist. The first approach would consist of hydrogenation of a ring at the end of the cluster, followed by ring opening and cracking to produce a derivative of the next lower member of the aromatic series. This procedure could be repeated, yielding ultimately one molecule of benzene derivative for each aromatic cluster thus utilized. The second approach may be the hydrogenation of a ring within the cluster other than an end ring, followed by cracking of this ring to yield two aromatic fragments. Completion of this procedure would yield at least two molecules of benzene or its derivatives for each cluster thus utilized.

In an effort to gain understanding of the basic principles involved, the study was initiated using pure compounds. The first compound investigated was anthracene, a fused, linear, three-ringed compound. The catalytic hydrocracking studies were then extended to 9,10-dihydroanthracene.

Experimental Procedure

The equipment consisted of an autoclave of one-liter capacity, equipped with a variable speed magnetic stirrer, a pressure gauge, and a thermocouple well. Auxiliary to the autoclave were a temperature recorder to follow the rate of heating, rheostats to assist in obtaining a smooth heating curve, and a temperature controller capable of maintaining constant temperature within $\pm$ 3°C.

The hydrogenation experiments were performed using 25 grams of anthracene of 98 percent purity, mixed with 2.5 grams of catalyst (nickel tungsten sulfide pellets of 1/8-inch diameter). The system was evacuated and then filled with hydrogen to a predetermined cold pressure such that the operating pressure at the temperature of the experiment would be 1500 p.s.i. Approximately 20 minutes were required to bring the system to operating temperature. Solid samples from the reaction products were dissolved in trichloroethylene and analyzed by means of a flame-ionization chromatograph, with an Apiezon-L separation column. Liquids and gases were analyzed by means of the gas chromatograph.

Studies concerning the continued reactions of the 9,10-dihydroanthracene at 510°C were performed using 25 grams of 9,10-dihydroanthracene of 95 percent purity, mixed with 2.5 grams of catalyst (Kaolin pellets of 1/8-inch diameter or fluid zeolite cracking catalyst). The techniques for hydrogenation and product analyses were similar to those described above.

Results and Discussion

Several parameters were investigated as they affect hydrogenation of anthracene. These parameters include temperature, hydrogen pressure, catalyst, and reaction time.

Typical curves from this study showing the rate of disappearance of anthracene during catalytic hydrogenation at various temperatures ranging from 220° to 435°C are shown in Figure 1. These data are presented as weight percent anthracene in the product as a function of time.

Figure 2 shows four chromatograms illustrating the progress of the reactions at 390°C. Hydrogenation of anthracene to 9,10-dihydroanthracene occurs readily. As the time increases, formation of 1,2,3,4-tetrahydroanthracene becomes appreciable. This is followed by formation of 1,2,3,4,5,6,7,8-octahydroanthracene with some naphthalene ultimately being formed.

Figure 3 shows four chromatograms which illustrate the progress of the hydrogenation reactions at comparable times as a function of temperature. At the lower temperatures, hydrogenation to 9,10-dihydroanthracene is essentially complete with only limited hydrogenation to higher stages. As temperature is increased, progressive hydrogenation to 1,2,3,4,-tetrahydroanthracene occurs, followed by hydrogenation to the octahydro-derivative, with hydrocracking to form naphthalene derivatives ensuing. At 435°C, further hydrogenation of these derivatives, followed by cracking to form benzene derivatives, becomes appreciable.

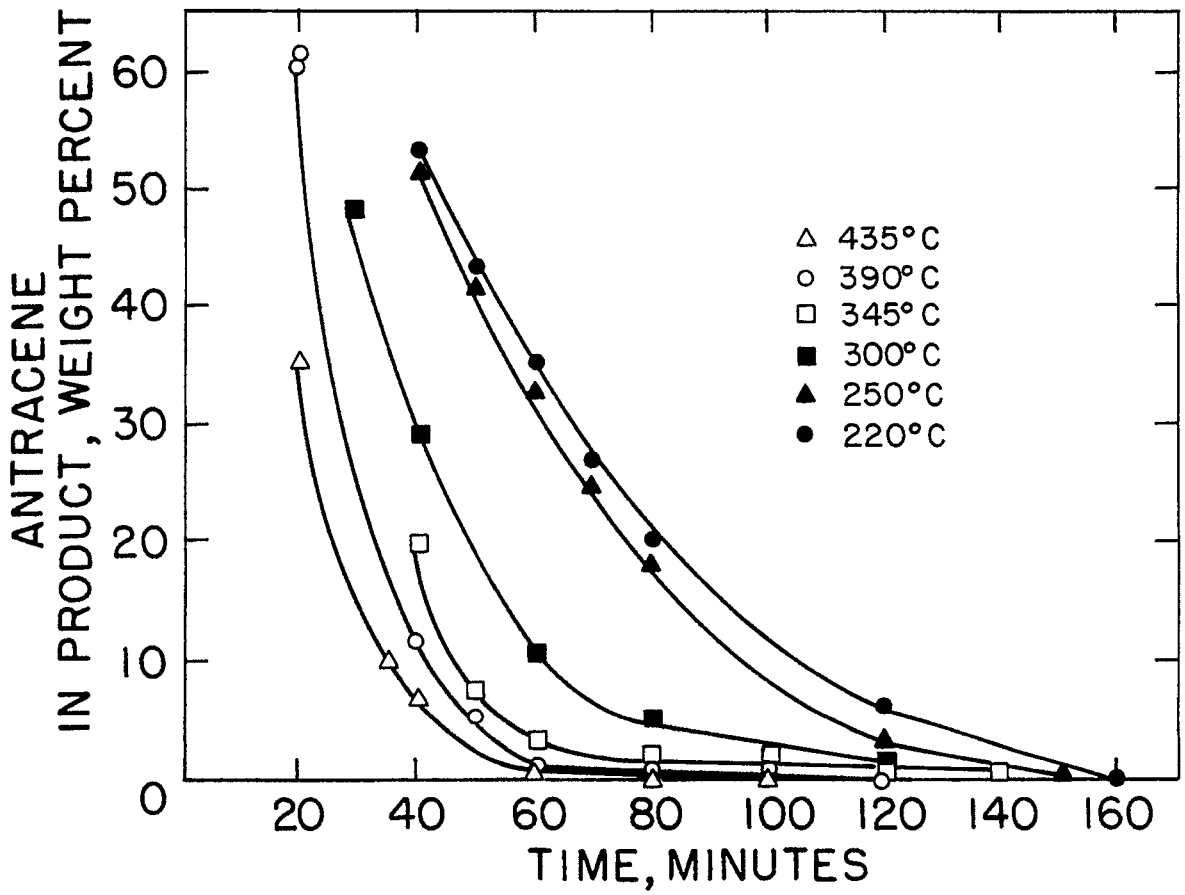

Figure 1. Rate of disappearance of anthracene during catalytic hyrogenation.

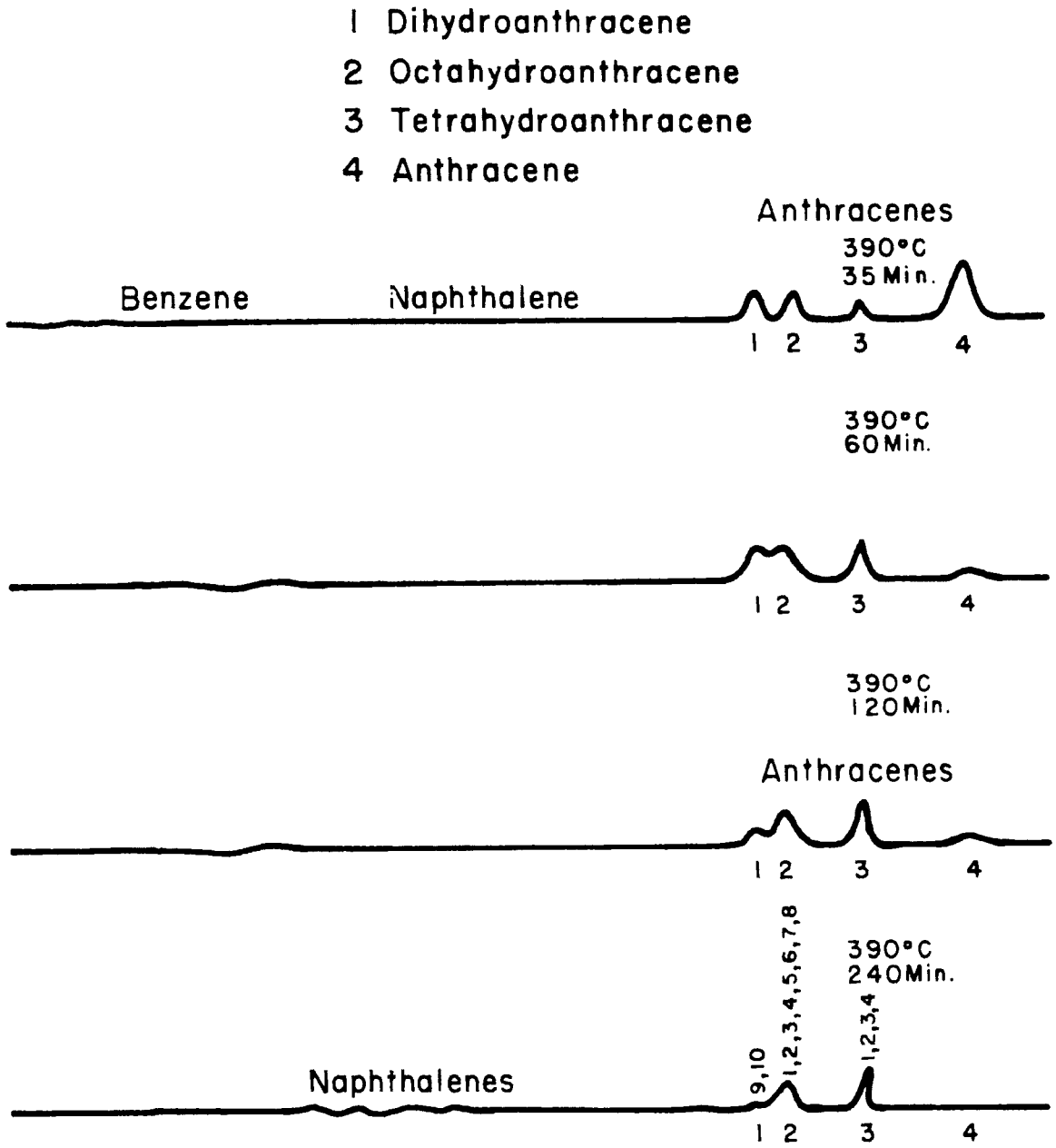

Figure 2. Chromatograms showing product distribution on hydrogenation of antracene at 390°C, 1500 psi, Ni-W-S catalyst.

1 Dihydroanthracene
2 Octahydroanthracene
3 Tetrahydroanthracene
4 Anthracene

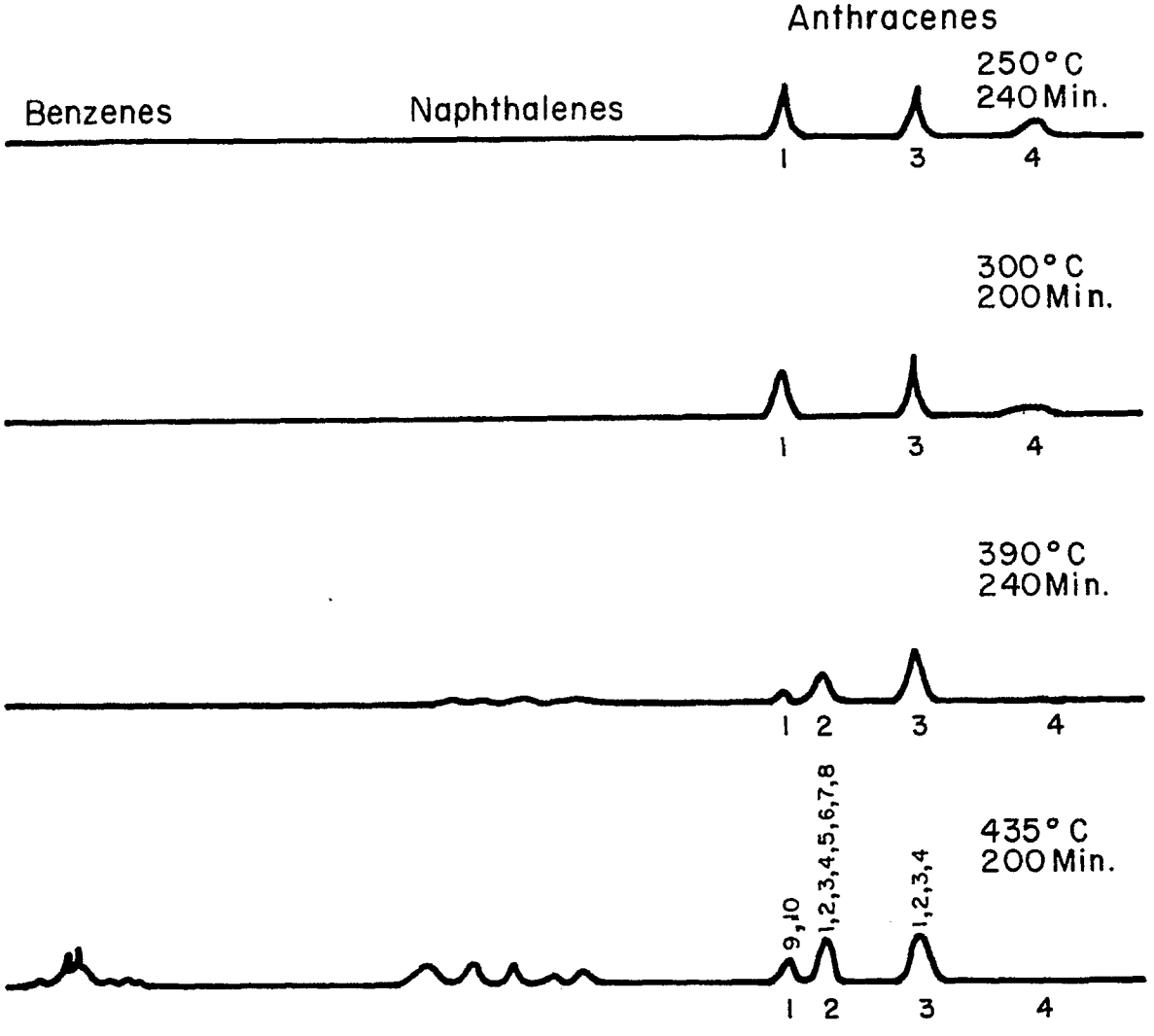

Figure 3. Chromatograms showing product distribution on hydrogenation of anthracene at 250°C to 435°C, 1500 psi.

At temperatures below 250°C, yields of 9,10-dihydroanthracene approaching 80 percent by weight may be obtained (Figure 4). Continued hydrogenation yields 1,2,3,4-tetrahydroanthracene accompanied by a loss of hydrogen from the 9 and 10 positions (Figure 5). Further hydrotreating of this product yields 1,2,3,4,5,6,7,8-octahydroanthracene (Figure 6), with cracking to naphthalene derivatives being concurrent with or subsequent to the formation of the octahydroanthracene (Figure 7). Continued hydrogenation of the naphthalene derivatives yields benzene derivatives and gases (Figure 8).

An analysis of the data at a particular temperature (e.g., 435°C) reveals that maximum quantities of the various hydrogenation products appear in the following order: 9,10-dihydroanthracene (about 40 minutes), 1,2,3,4-tetrahydroanthracene (about 100 minutes), and 1,2,3,4,5,6,7,8-octahydroanthracene (about 140 minutes). The appearance of naphthalene derivatives is subsequent to or concurrent with the appearance of the octahydroanthracene, suggesting that the ring opening reactions to produce the naphthalene derivatives may occur primarily on the octahydro-derivative of anthracene under the conditions of these investigations.

Progress of the hydrocracking reactions at 510°C using Kaolin cracking catalyst and 9,10-dihydroanthracene as the raw material is readily observed in Figure 9. Hydrogenation to 1,2,3,4-tetrahydroanthracene was accompanied initially by dehydrogenation of form some anthracene due to the equilibria involving these three compounds. It is not known whether the Kaolin catalyst permits direct hydrocracking of the 1,2,3,4-derivative of anthracene or whether the hydrocracking of the octahydro-derivative proceeds very rapidly in the early stages. At 240 minutes, the naphthalene derivatives amounted to approximately 44 weight percent and the benzene derivatives approximately 18 weight percent of the total product.

Hydrogenation of anthracene is observed to be first order with respect to anthracene concentration (Figure 10), with an activation enthalpy of 3.8 kilocalories per mole and an activation entropy of -58 entropy units (Figure 11).

A reaction occurring at a catalyst surface will, in general, include the following steps: diffusion of the reactants to the surface, orientation and adsorption on the surface, reaction on the surface, desorption of the reaction products from the surface, and diffusion of the products away from the surface. The slowest of these steps will determine the rate of the overall process. Consideration of the enthalpy and entropy of activation led to the conclusion that the rate-controlling step involves the orientation and adsorption of the reacting molecules on the catalyst surface.

The various positions on the multiring aromatic molecule manifest different degrees of reactivity. Hence, anthracene was observed in this study (as well as by other investigators) to add hydrogen in the 9 and 10 positions to form the dihydride, producing yields of this compound as high as 80 percent by weight under carefully controlled conditions.

The addition of hydrogen in the 9 and 10 positions of the anthracene molecule (and in comparable positions away from an end ring on the higher

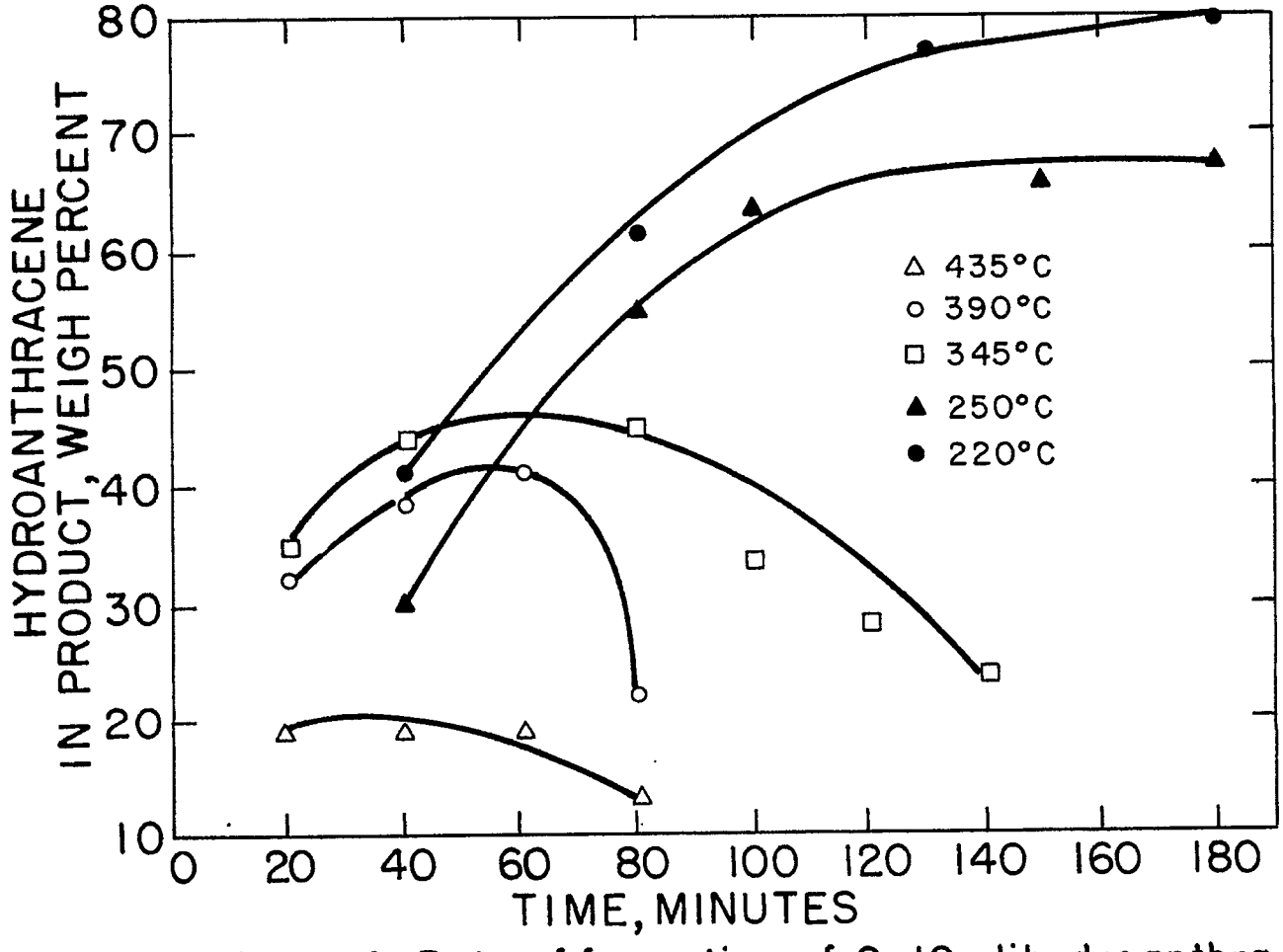

Figure 4. Rate of formation of 9-10 dihydroanthracene during catalytic hydrogenation of anthracene.

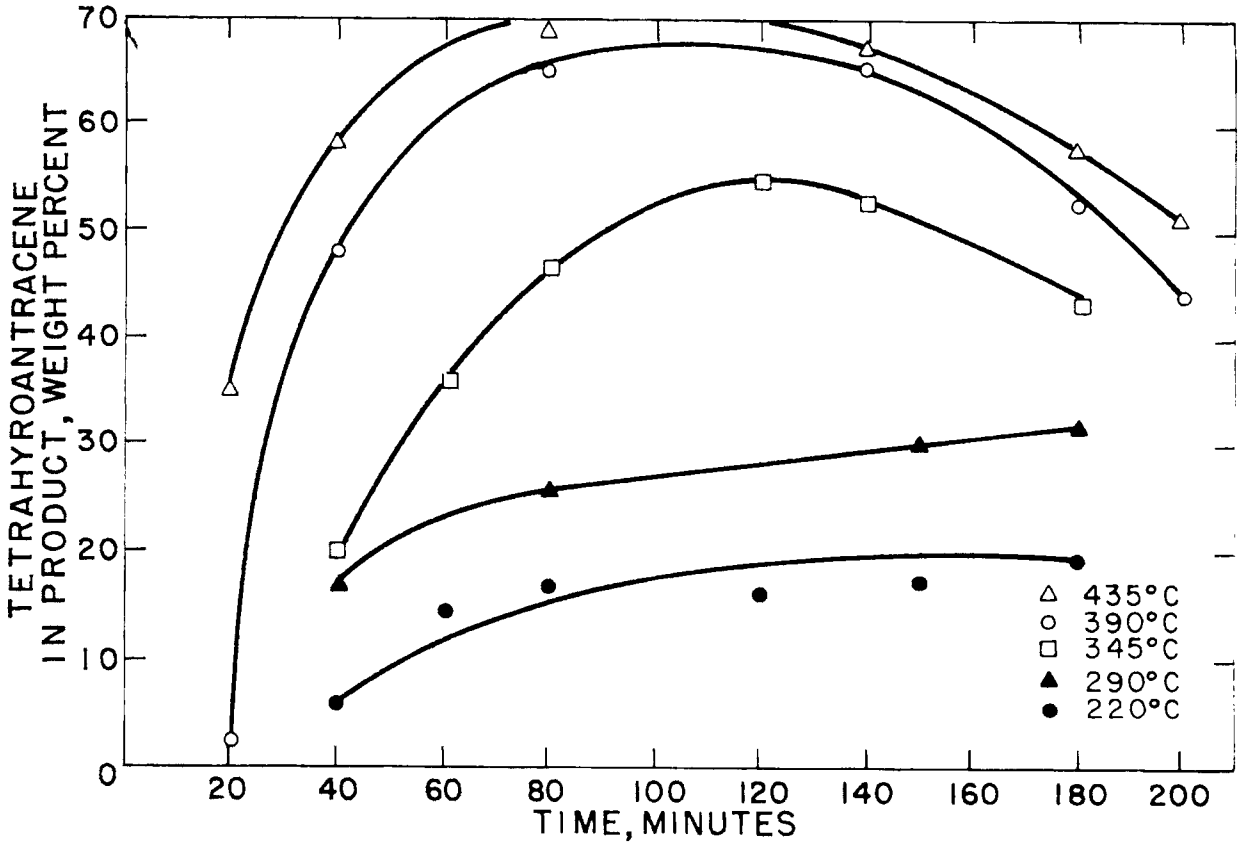

Figure 5. Rate of formation of 1,2,3,4-tetrahydroanthracene during hydrogenation of anthracene.

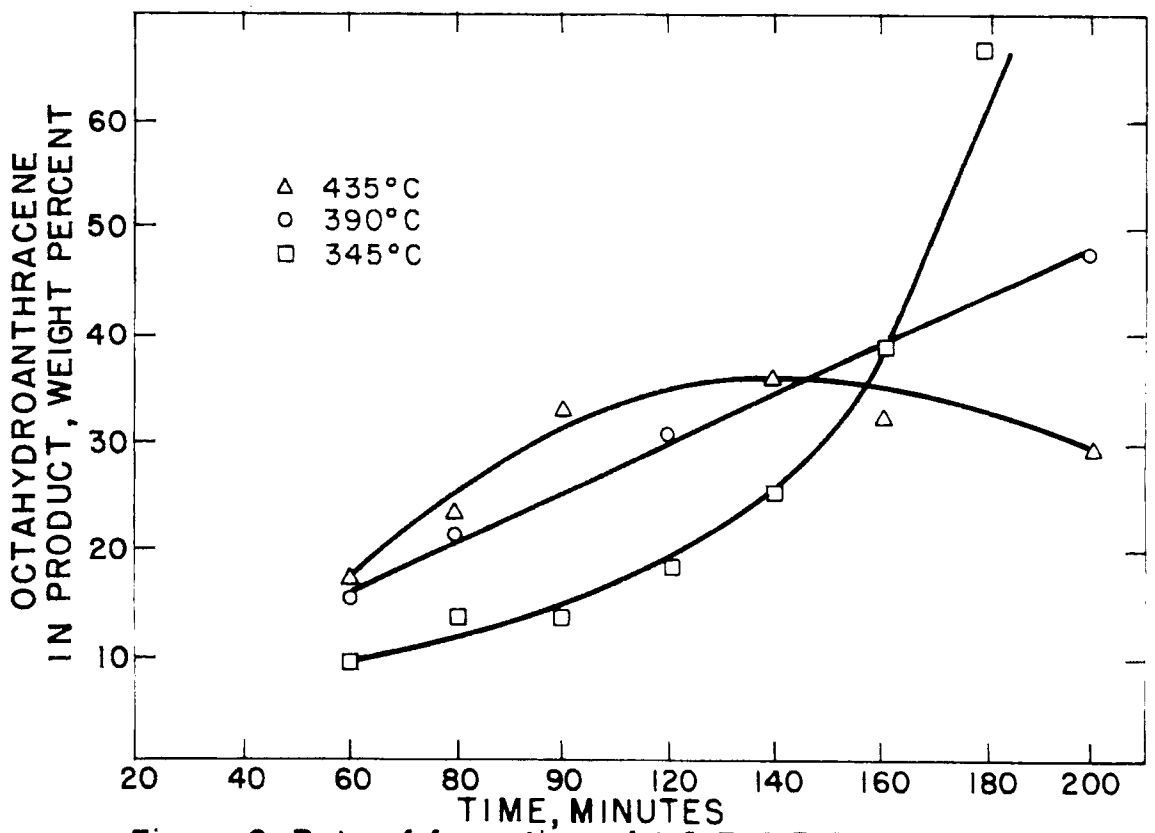

Figure 6. Rate of formation of 1,2,3,4,5,6,7,8-octahydroanthracene during hydrogenation of anthracene.

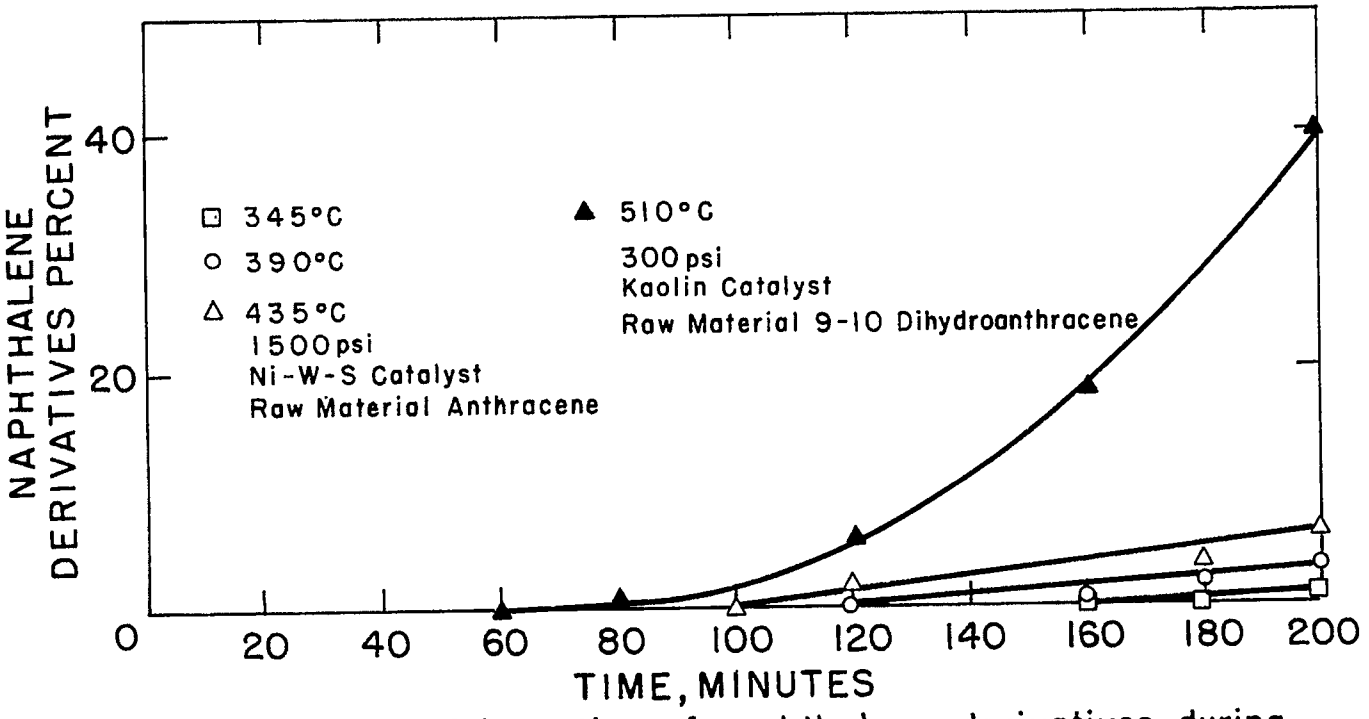

Figure 7. Rate of formation of naphthalene derivatives during hydrogenation and hydrocracking.

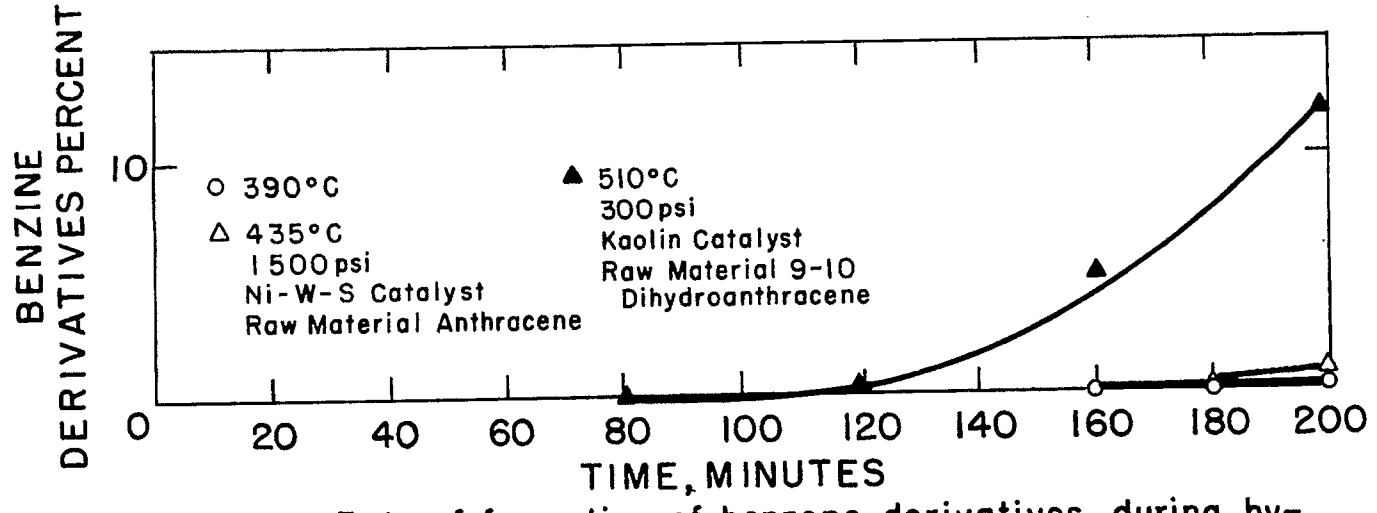

Figure 8. Rate of formation of benzene derivatives during hydrogenation and hydrocracking.

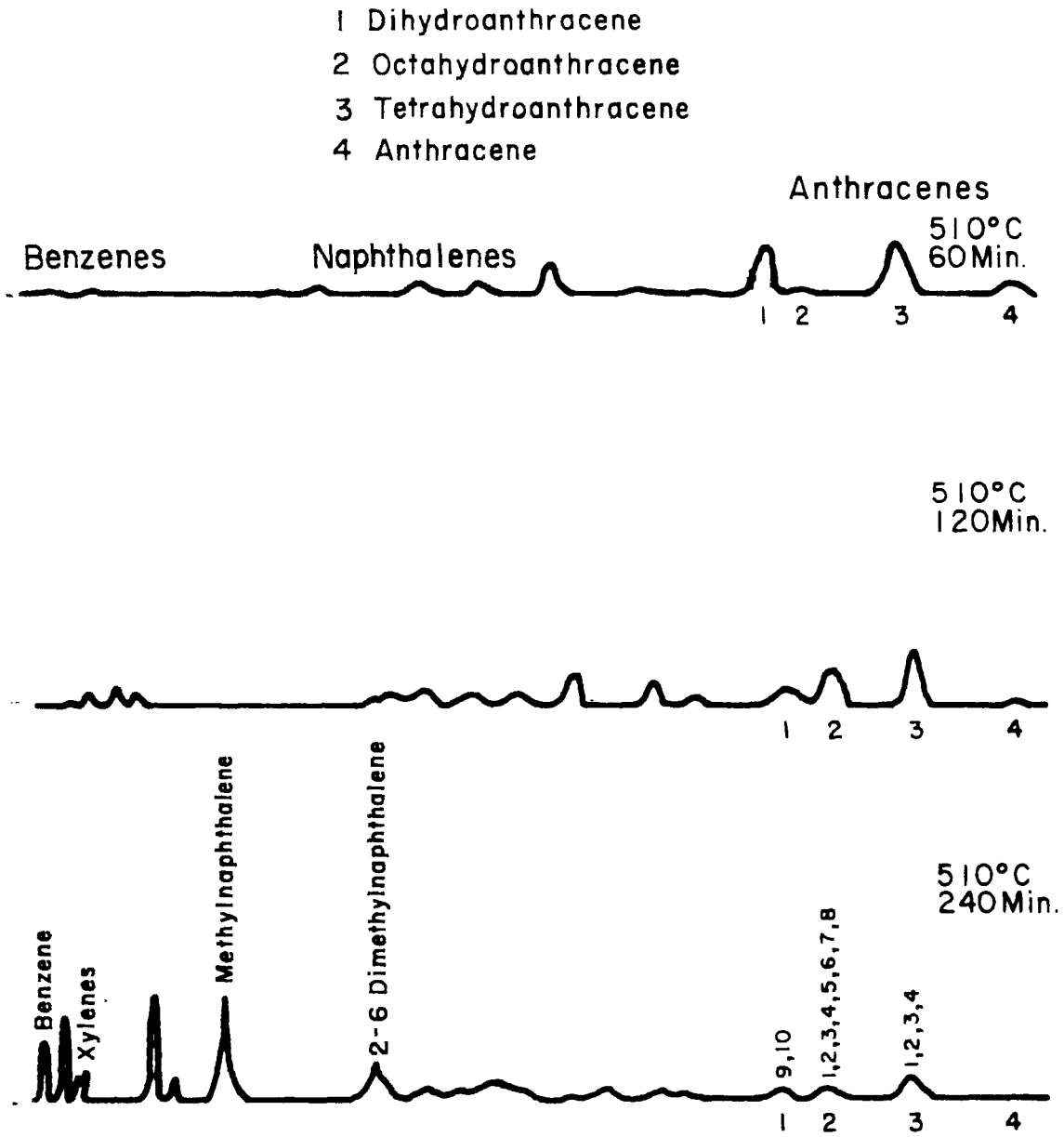

Figure 9. Chromatograms showing product distribution on cracking 9-10 dihydroanthracene, 510°C, 300 psi.

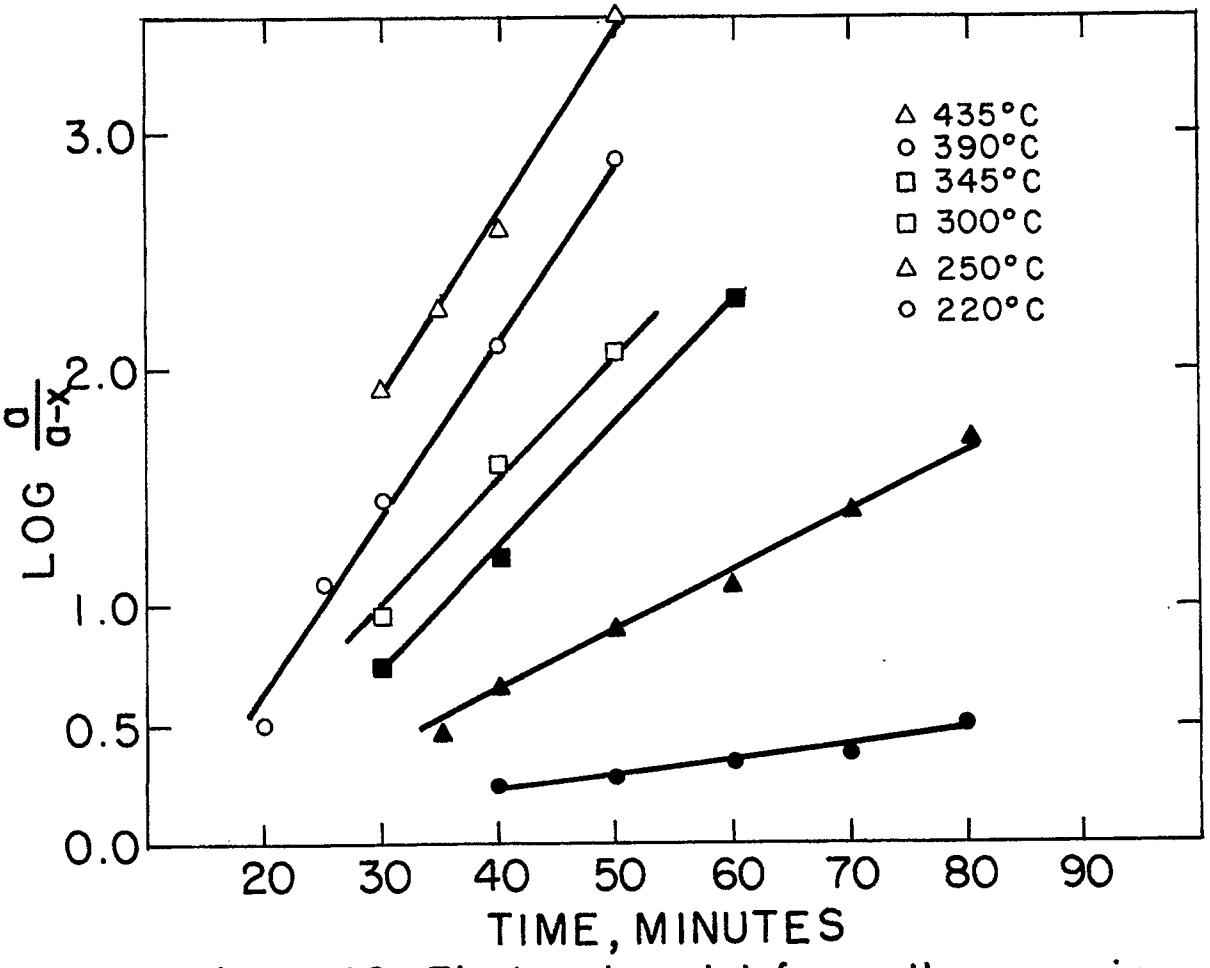

Figure 10. First order plot for anthracene in product during hydrogenation of anthracene.

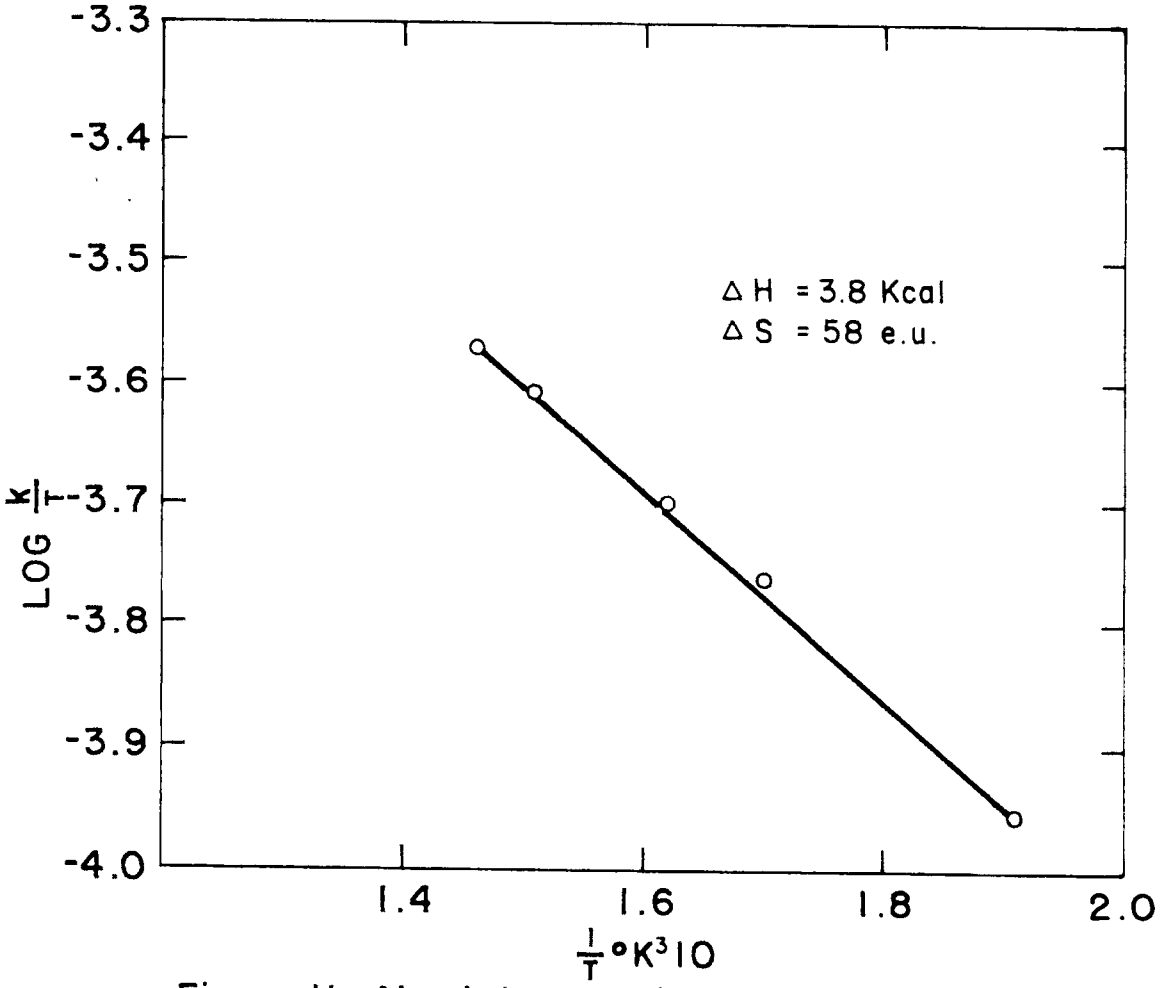

Figure II. Absolute reaction rate plot of hydrogenation of anthracene.

aromatic homologues) would alter the aromatic nature of the bonds adjacent to these positions. One might expect a reduction in the resonance energy of the electrons associated with these bonds due to this alteration in aromatic nature, with resulting weakening and lengthening of the bonds. It would then be theoretically possible to rupture these bonds in preference to other bonds within the fused structure. To date, such a rupture has not been observed to occur. Attempts to catalytically hydrocrack the 9,10-dihydroanthracene resulted in hydrogenation in the 1,2,3,4 positions with an accompanying shift of hydrogen from the 9 and 10 positions. This shift is probably associated with the change in electron orbitals incident to the removal of the aromaticity of the ring involving the 1,2,3,4 positions.

Experiments were performed wherein the 9,10-dihydroanthracene was heated in an evacuated system in the absence of hydrogen. The result was a reduction in the amount of the dihydride, accompanied by formation of anthracene and 1,2,3,4-tetrahydroanthracene. An increase in temperature produced dehydrogenation in the 9 and 10 positions of the dihydride, the hydrogen thus produced evidently being utilized to hydrogenate the end ring of some of the molecules.

It appears that with the use of the catalysts of this study, the temperature required for cracking the central ring of the 9,10-dihydroanthracene is higher than that required for dehydrogenation of this material, thus favoring the dehydrogenation with concurrent or subsequent hydrogenation of the end ring. It seems evident that more appropriate catalysts must be developed for this particular reaction if success is to be achieved. Such a catalyst would appreciably reduce the activation energy for hydrocracking the dihydroanthracene bonds adjacent to the 9 and 10 positions without aiding the hydrogenation or dehydrogenation reactions.

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Projects VI and XI. EVALUATION AND TREATING OF COAL DERIVED LIQUIDS

The efficient conversion of coal oils to gasoline depends upon the nature of the coal oils, the type of processing employed, the activity and the selectivity of the catalysts and the type of reactor systems employed. All these aspects were investigated.

The Coal Oils (Feed Stocks)

Two types of coal derived oils were used as feed stocks. One of the oils was obtained by carbonizing coal at 550° to 600°C in a laboratory oven

and the other oil was produced by coal hydrogenation. Gas oil was used for making a comparative evaluation. The coal oils used were almost similar in their properties. The above mentioned feed stocks were hydrorefined and hydrocracked under different reaction conditions to get the products. The coal oils produced by pyrolysis and solvent treatment have to be processed in a similar way. The coal hydrogenation oil has to be split into a distillate fraction and a residual fraction and each fraction has to be processed separately.

Processing of Coal Oils (Hydrorefining and Hydrocracking)

The hydrorefining and hydrocracking of the coal oils were carried out in batch autoclaves, fixed bed reactors and ebulating bed systems. A temperature range of 350° - 500°C and hydrogen pressure from 500 to 3000 psi were tried and the product distribution was studied. The kinetic work was done on both batch and fixed bed systems and the reactions were found to be of second order, first order with respect to the coal oil and first order with respect to hydrogen concentration. The rates of removal of S, O and N from coal oil in hydrorefining were found to be consistent with equations i to v.

$$k_s = 2 \times 10^2 \, e^{-11000/RT} \ min^{-1} \qquad (i)$$

$$k_{o_1} = 6 \times 10^6 \, e^{-12000/RT} \ min^{-1} \ (300° \text{ to } 400°C \text{ range}) \qquad (ii)$$

$$k_{o_2} = 3 \times 10^5 \, e^{-8000/RT} \ min^{-1} \ (400° \text{ to } 500°C \text{ range}) \qquad (iii)$$

$$k_{n_1} = 1 \times 10^6 \, e^{-10000/RT} \ min^{-1} \ (300° \text{ to } 400°C \text{ range}) \qquad (iv)$$

$$k_{n_2} = 3 \times 10^{11} \, e^{-14000/RT} \ min^{-1} \ (400° \text{ to } 500°C \text{ range}) \qquad (v)$$

where k_s, k_{o_1}, k_{o_2} and k_{n_1}, k_{n_2} are the rate constants for desulfurization, deoxygenation and denitrogenation respectively. The rates of hydrocracking were found to be consistent with the equations vi to ix.

$$k_g = 0.17 \times 10^6 \, e^{-17,600/RT} \ hrs^{-1} \qquad (vi)$$

$$k_s = 0.21 \times 10^5 \, e^{-14,500/RT} \ hrs^{-1} \qquad (vii)$$

$$k_o = 0.36 \times 10^5 \, e^{-13,600/RT} \ hrs^{-1} \qquad (viii)$$

$$k_n = 0.47 \times 10^5 \, e^{-15,900/RT} \ hrs^{-1} \qquad (ix)$$

where k_g is the rate constant for gasoline formation.

The cracking reactions involving the seission of C - C, C - S, C - O, and C - N bonds were found to be rate limiting. Based on the data, the mechanisms of hydrorefining and hydrocracking of coal oils were proposed. The product distribution data obtained on both the batch and fixed bed systems were normalized and the hydrogen requirements were calculated. A temperature of about 425° to 430°C and a pressure of 1500 psi were found to be optimum for hydrorefining and a temperature of about 470° to 480°C and a pressure of about 2000 to 2500 psi were found to be the optimum for hydrocracking. The data given in Table I were obtained under optimum conditions.

TABLE I

MATERIAL BALANCE

(Feed: Coal oil, 100 Bbl., Hydrogen, 1,134 lbs.)

Product	Yield
Gasoline, bbl	70
Diesel oil, bbl	14
Refinery gas, cu. ft.	32,500
Solid fuel, tons	1.4
Water, gallons	84
Hydrogen Sulfide, cu. ft.	2,500
Ammonia, lbs.	270

Based on the data, a conceptual scheme for the production of gasoline, diesel oil and jet fuel was proposed. The work has to be done in different stages and with different coal oil fractions for optimization purposes.

The Catalysts

Pure grade molybdenum disulfide, cobalt-molybdate and sulfides of nickel and tungsten on alumina were used for hydrorefining work. Duel-functional catalysts containing oxides and sulfides of Co, Mo, Ni and W on silica-alumina were used for hydrocracking. All the catalysts used were commercial products designed for petroleum refining. Though these catalysts can be used for coal oil processing, they are not the best. The selectivity is not enough for the removal of oxygen compound and hydrogenation of aromatics, which are the most predominant components of coal oils. New catalysts compositions have to be developed with adequate selectivity to suit the coal oil processing. Work is under way for the development of suitable catalysts based on both silica-alumina and molecular sieves. The success of this work may lead to further improvement of the product distribution data.

Catalyst Life

The consumption of the catalyst in the process is an important factor. Coke deposition on the catalyst is one of the factors which reduces the life of the catalyst. This aspect was studied to some extent and it was found that excessive Coke deposition occurs during hydrocracking of the coal oil. However, the Coke deposition can be minimized by carrying out the process in two stages. Much more work has to be done to determine the catalyst consumption in the process.

The Reactor Systems: Three types of reactor systems were used.

Batch autoclaves. The batch system was used mainly for kinetic studies and for the evaluation of the activity and selectivity of the catalysts. This system was also used for calculating hydrogen requirements at different levels of conversion.

Continuous fixed bed reactor systems. The fixed bed system was used both for the kinetic and product distribution studies. Distillates oils were processed in this system. This system is not quite suitable for the processing of the whole oils. However, deasphalted crude coal oil was successfully processed though it gave rise to excessive coke deposition on the catalyst. However, this system is the most versatile for the processing of distillate oils.

Continuous ebulating bed reactor system. This system was used for the hydrorefining and hydrocracking of coal oil distillates to start with. An evaluation of the relative efficiencies of the fixed and ebulating bed systems was made. This system can be used both for the processing of whole oils or residual fractions of the oils. Work is under way on the processing of whole coal oils and residual fractions of the coal oils. The design of the ebulating bed reactor has to be further improved. Design of an ebulating bed reactor system based on a different principle is undertaken.

Project VIII. STUDIES OF COAL REACTIONS IN CONJUNCTION WITH MICROWAVE RADIATION

The reactions of coal at high temperatures have been studied by a number of techniques. These include flash photolysis, arc-image heating, reaction with a plasma, laser irradiation and very rapid pyrolysis. The products of very high-temperature reactions are significantly different from those of conventional carbonization. The formation of acetylene, hydrogen, and carbon monoxide are favored at high temperatures and the yield of tar is decreased. Ladner has reviewed the high-temperature pyrolysis of coal by various techniques[1]. Recent developments in coal processing have included studies of high-temperature processing using an induction plasma and electrical discharges.

A study of coal in a microwave discharge was undertaken to learn more about the physical properties of coal and the reactions that it undergoes. The microwave system can be used to heat the coal directly or to generate a plasma from a number of gases or mixtures of gases. By studying the reaction products and by varying the nature of the coal and its pretreatment and th nature of the plasma, one can learn much about the reactions of coal. Blaustein and Fu haye reported some results of the reactions of coal in a microwave plasma[2].

The microwave system has just been completed and experimental results are not yet available. This work will be continued. The microwave system consists of a Raytheon Model PGM-100 microwave power generator with a tuning section and a tapered power-focusing section. It has a maximum power output of 800 watts and operates at a frequency of 2450 MH_2. A glass vacuum system has been constructed to handle reactant and product gases. Samples will be collected for analysis by conventional methods. A Tracerlab LTA-300 Low Temperature Asher is also available for plasma studies. It has been used to ash a number of coal samples using an oxygen plasma. The ash content determined by this method is higher than that obtained by ASTM tests. The infrared adsorption patterns of the ashes are similar.

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Project IX. HIGH PRESSURE DTA OF COAL

Differential thermal analysis, DTA, is a technique that has been widely used to determine phase changes and chemical reactions in chemical systems. In a DTA experiment, a sample and an inert reference material are heated or cooled at a controlled rate. Thermal gradients are generated in both sample and reference. The gradient will depend on the specific heat, thermal conductivity, density, and particle size of the sample and reference and on the heating rate and geometry of the system. The temperature difference between sample and reference is recorded as a function of temperature. In the absence of reactions or transitions, a baseline is established. Endothermic or exothermic processes cause the thermal gradient of the sample to change and thus appear as endothermic or exothermic peaks in the temperature difference recording.

Several investigators have used DTA to examine coal samples. Howard has reviewed the DTA of coal[1]. Both exothermic and endothermic peaks have been reported and it is difficult to compare results. The results are

strongly dependent on the coal samples used and on the experimental conditions.

A high-volatile bituminous coal (Spring Canyon, 47% volatile matter) and a sub-bituminous coal (Big Horn, 46% volatile matter) were investigated by DTA. A Fisher Model 360 Differential Thermal Analyzer was used for DTA at atmospheric pressure. The sample consisted of approximately 50 mg of -60 mesh coal and Al_2O_3 was used as a reference. Samples were heated at 5°C/min.; the sub-bituminous coal show an endothermic peak at about 110°C due to loss of water and exothermic peaks at about 215°C, 460°C, and 680°C. In the absence of oxygen, the 213°C and 460°C peaks disappear and the 680°C peak is shifted to higher temperatures. The high-volatile bituminous coal shows exothermic peaks at about 60°C and 520°C. These peaks are shifted to slightly higher temperatures in the absence of oxygen. The peaks are broad and show some variation in duplicate runs.

DTA at pressures up to 20 k bars was performed using a cubic press. Temperature programming was accomplished with constant temperature regulator with a motor-driven set point. Linear heating at rates between 5°C and 20°C per minute were possible. A cylindrical sample was placed in the center of a pyrophyllite cube and surrounded by a nickel resistance strip used to heat the sample. A thermocouple in the center of the sample measured the temperature and was compared with a thermocouple in the pyrophyllite to obtain the temperature difference. The temperature was recorded and the temperature difference between sample and pyrophyllite reference material was amplified with a high gain d.c. amplifier and recorded. Many difficulties were encountered in the operation of the high-pressure DTA. Thermocouple and heating strip leads were sheared during pressurization and the samples were distorted making it difficult to maintain a matching geometry for sample and reference material. There were no indications of any significant deviations in the DTA of coal at high pressure from the DTA at atmospheric pressure.

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