



Reduction of sub-bituminous coal and lignite using carbon monoxide
by Wayne Jason York

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY in Chemical Engineering
Montana State University
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Abstract:

The reduction of a sub-bituminous coal and three lignites, using CO rather than H₂ was investigated. The sub-bituminous coal was mined at Colstrip, Montana, and the three lignites were mined at Savage, Montana, and Stanton and Noonan, North Dakota. The equipment in this study consisted of a 500 ml., rocking autoclave which operated between 380°C and 450°C, and a maximum operating pressure of 5000 psi. The analyses which were made included the conversion of the MAF coal to benzene soluble material, gas analyses of the reaction gases, and ultimate analyses and molecular weight determinations of the liquefied coal.

The results show that increasing pressure and temperature increase conversion, however, hydrocarbon gas production increases with temperature as well. The best solvent that was investigated for lignite was a mixture of alpha-naphthol and phenanthrene, and for sub-bituminous it was anthracene oil. Grinding the coal in a mortar and pestle produced better conversion results than pulverized coal because the coal was less oxidized in the former grinding method. Noonan lignite is more reactive than Stanton lignite, which in turn is more reactive than Savage lignite.

The reason for these differences has been attributed to the composition of the ash in the coal. Na₂CO₃ was studied as a catalyst for the liquefaction of coal using CO, with quite successful results.

The tar product obtained from the coal has a hydrogen-to-carbon ratio of about 1.1 and an ash content of less than 0.1% compared to coal's hydrogen-to-carbon ratio of 0.8 and 7% ash. This product would be an ideal fuel for magneto-hydrodynamics, and will overcome many of the obstacles that have prevented magnetohydrodynamics from becoming a reality.

TSR processes utilizing the liquefaction of coal using CO were designed and studied economically. One process produces CO from char, H₂O and O₂, while the other produces the CO from CO₂ and the char. The first process is competitive with existing liquefaction processes using hydrogen, and the second process is more economically attractive than any liquefaction process that has been proposed for the production of tar products.

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Approved:

Lloyd Bengtson
Head, Major Department

Lloyd Bengtson
Chairman, Examining Committee

Henry L. Parsons
Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

June, 1971

ACKNOWLEDGMENT

The author wishes to thank the staff of the Chemical Engineering Department of Montana State University for their suggestions and criticisms which led to the completion of this project. Special thanks goes to Dr. Lloyd Berg, director of this research, for his guidance throughout this investigation. In addition, Dr. Jack Olson is given acknowledgment for sharing with me in the early phases of my project his knowledge of coal research. Cooperation from my fellow researcher, Nguyen Dat, has been appreciated.

The author is also indebted to the Office of Education and to the Chemical Engineering Department of Montana State University for their financial support and for being given the opportunity to conduct this investigation. Financial support by the Montana Coal Resources Research Council for equipment and chemicals is gratefully acknowledged.

The coal was supplied by Montana Power, Montana Dakota Utilites, Basin Electric Cooperative, and Baukol-Noonan. Analyses of fuel oil and asphalt were performed by Esso Research and Engineering and many coal analyses

were supplied by the Bureau of Mines at Grand Forks, North Dakota.

Finally, the author wishes to thank his family and his wife for their encouragement and support.

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ABSTRACT

The reduction of a sub-bituminous coal and three lignites using CO rather than H_2 was investigated. The sub-bituminous coal was mined at Colstrip, Montana, and the three lignites were mined at Savage, Montana, and Stanton and Noonan, North Dakota. The equipment in this study consisted of a 500 ml. rocking autoclave which operated between $380^{\circ}C$ and $450^{\circ}C$, and a maximum operating pressure of 5000 psi. The analyses which were made included the conversion of the MAF coal to benzene soluble material, gas analyses of the reaction gases, and ultimate analyses and molecular weight determinations of the liquefied coal.

The results show that increasing pressure and temperature increase conversion, however, hydrocarbon gas production increases with temperature as well. The best solvent that was investigated for lignite was a mixture of alpha-naphthol and phenanthrene, and for sub-bituminous it was anthracene oil. Grinding the coal in a mortar and pestle produced better conversion results than pulverized coal because the coal was less oxidized in the former grinding method. Noonan lignite is more reactive than Stanton lignite, which in turn is more reactive than Savage lignite. The reason for these differences has been attributed to the composition of the ash in the coal. Na_2CO_3 was studied as a catalyst for the liquefaction of coal using CO with quite successful results.

The tar product obtained from the coal has a hydrogen-to-carbon ratio of about 1.1 and an ash content of less than 0.1% compared to coal's hydrogen-to-carbon ratio of 0.8 and 7% ash. This product would be an ideal fuel for magneto-hydrodynamics, and will overcome many of the obstacles that have prevented magnetohydrodynamics from becoming a reality.

Two processes utilizing the liquefaction of coal using CO were designed and studied economically. One process produces CO from char, H_2O and O_2 , while the other produces the CO from CO_2 and the char. The first process is competitive with existing liquefaction processes using hydrogen, and the second process is more economically attractive than any liquefaction process that has been proposed for the production of tar products.

II. INTRODUCTION

A. United States Energy Requirements

Only until recently have we been able to keep pace with our country's insatiable appetite for energy. For the first time in our history in 1970, there was considerable discussion of power shortages. There are many reasons for the shortages, but the major factors are: the overselling of nuclear energy, mine safety laws which result in the closing of coal mines, coal exports, pollution control, and Middle East oil import curtailments (1).

Not only must we supplement present shortages of fuel, but we must supply the expected increase of fuel requirements in the years to come. Since 1880, the United States' energy consumption has doubled every 30 years and it is expected to do so again in the next 20 to 25 years. Even more important, the United States' power consumption has been doubling every eight to ten years. Based on these predictions, we will require well over 125 quadrillion BTUs of energy in the year 2000 (2). This increase is due to the population increase and the per capita increase in energy consumption.

In addition to the growth problem, we are now facing

the possibility of shortages in presently used fuels. For example, the natural gas and petroleum reserves-to-consumption ratios have been decreasing for the last several years, and even the Alaskan oil find will not replace the expected shortages (3,4). Known recoverable United States reserves of oil, gas, and uranium each could supply about 300 quadrillion BTUs of energy or a total of 900 quadrillion BTUs. About ten percent of the fossil fuel consumption is also used as a feed stock for the organic chemical industry. Because of the increase in future energy requirements and the potential shortages of presently used fuels, we must obviously find new and more efficient ways of producing energy and organic chemicals.

The most desirable solution to this problem would be atomic fusion, and at this time the Atomic Energy Commission is convinced that fusion-power reactors are not blocked by laws of nature. "Depending on one's underlying assumptions, or the level of the effort and the difficulties ahead, the time it would take to produce a large prototype could range from as much as 50 years to as little as ten years (5)." This would indicate that commercial hydrogen-powered reactors may be developed by the turn of the century, which is much too long to wait for a suitable

solution to the energy problems for the near future. Breeder reactors, which will make more efficient use of nuclear fuels, are more promising and may be used on a commercial scale by 1984 (6).

B. Fossil Fuel Potential

Fossil fuels will continue to play a very important role in satisfying our energy demands, particularly in the transportation sector. More efficient methods of generating electricity from fossil fuels, and new processes to utilize or convert heretofore unused fossil fuels into usable fuels will have to be investigated. The three major sources of these fuels are coal, tar sands, and oil shale, but each offers advantages and disadvantages.

The advantage of tar sands is that the oil is easy to extract from the sand. The oil after extraction requires only small amounts of hydrogen to obtain a synthetic crude oil. Tar sands are undesirable in that they are located in northern Canada, which is a considerable distance from markets in the United States. The ore contains only 15 percent carbon, but nonetheless Sun Oil Corporation has a 45,000 bbl/day plant processing tar sands.

Oil shale technology is fairly well developed and the

reserves are fairly large (they contain about 80 billion barrels of oil). Unfortunately, the crude oil is of rather poor quality and the shale oil reserves are not close to processing water sources.

When compared to other fossil fuels, we note that there are huge reserves of coal in the United States, or about 4,600 quadrillion BTUs. Coal reserves are a short distance from market; are cheap to obtain in many areas, and provide a great versatility of uses. However, the big disadvantage is that technology has not been fully developed in order to make use of many of coal's potentials. Thus, with future improvements in coal technology, and with utilization of its vast reserves and versatility, coal will play a major role in supplying energy for the future. Factors, other than technological factors, which will dictate when coal will be used for the production of hydrogenated coal products include: cost of money, taxes on mineral extraction, assigning of royalties for coal leases, and guidelines for oil import quotas (7).

One of the largest reserves of coal in the world is the Fort Union formation (Figure 1). It contains about 700 billion tons of sub-bituminous coal and lignite, or about seven percent of the world's known reserves (25

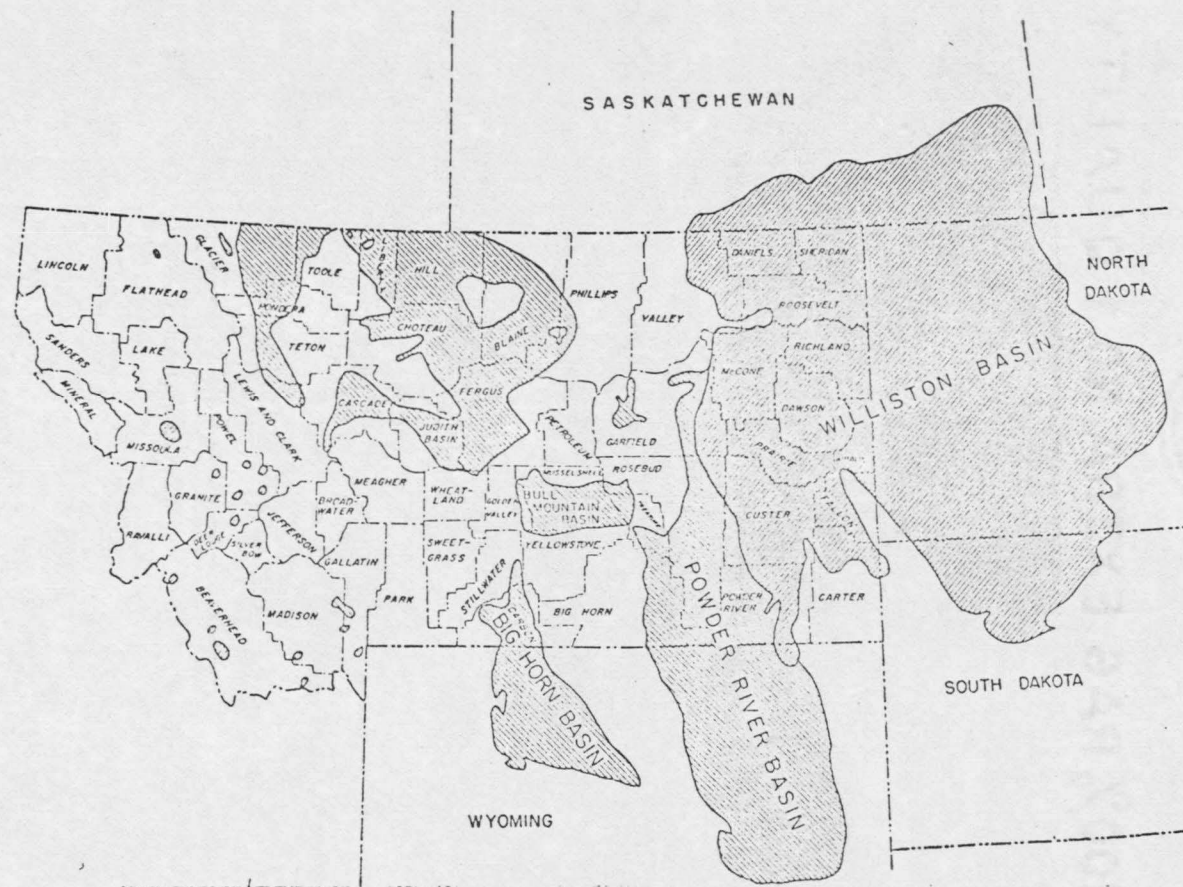


Figure 1. The Fort Union Coal Region in Montana and Adjacent States. Also shows other coal areas in Montana. (8)

percent of the United States' reserves). Montana shares about 220 billion tons of this coal, of which about 20 billion tons can be strip mined economically today.

The Fort Union coal will probably have four major uses before the turn of the century. It will be liquefied, gasified, used to obtain chemicals, and burned for electric power generation. In fact many elaborate systems utilizing these processes have been proposed (9,10).

Liquefaction to gasoline, aviation fuel, and synthetic crude oil has been studied for many years. Because of its importance to the direction that this project took, the historical developments of liquefaction will be discussed in the next chapter. Chemicals and carbon products are produced from coal by essentially the same methods as liquefaction. During the early 1950's, Union Carbide had a large pilot plant in West Virginia to obtain chemical feeds, but the Bergius process that they used proved to be uneconomical (11). New concepts of obtaining chemicals from coal via hydrogenation have since been proposed (12).

Gasification is becoming increasingly important and a great deal of research is being conducted in the United States (13,14,15). The processes are designed to replace natural gas with a high BTU gas containing mostly methane.

Many oil companies have realized the importance of coal, particularly in the Fort Union region. Consolidation Coal Company merged with Continental Oil; Pittsburgh and Midway Coal Company with Gulf Oil Corporation, and Island Creek Coal Company merged with Occidental Petroleum. In addition, Standard Oil of New Jersey has spent 25 million dollars leasing coal land in Illinois, Montana, and Wyoming (16). Shell Oil has bought coal leases in Montana as well.

Producing electricity from coal is already a big business in Montana and the surrounding states. A new process for generating electricity from fossil fuels, which is currently being studied by the Avco Corporation, promises to be more efficient, thereby producing less pollution than the conventional steam generating method. This new method is called magnetohydrodynamics (MHD). The details of the operation are given in several articles (17,18), and need not be given here. However, some general discussion of the process will be given in order to orient the reader to some aspects of the process.

A simple diagram of the MHD system is shown in Figure 2. As in the steam generating method, a conductor must be passed through a magnetic field in order to

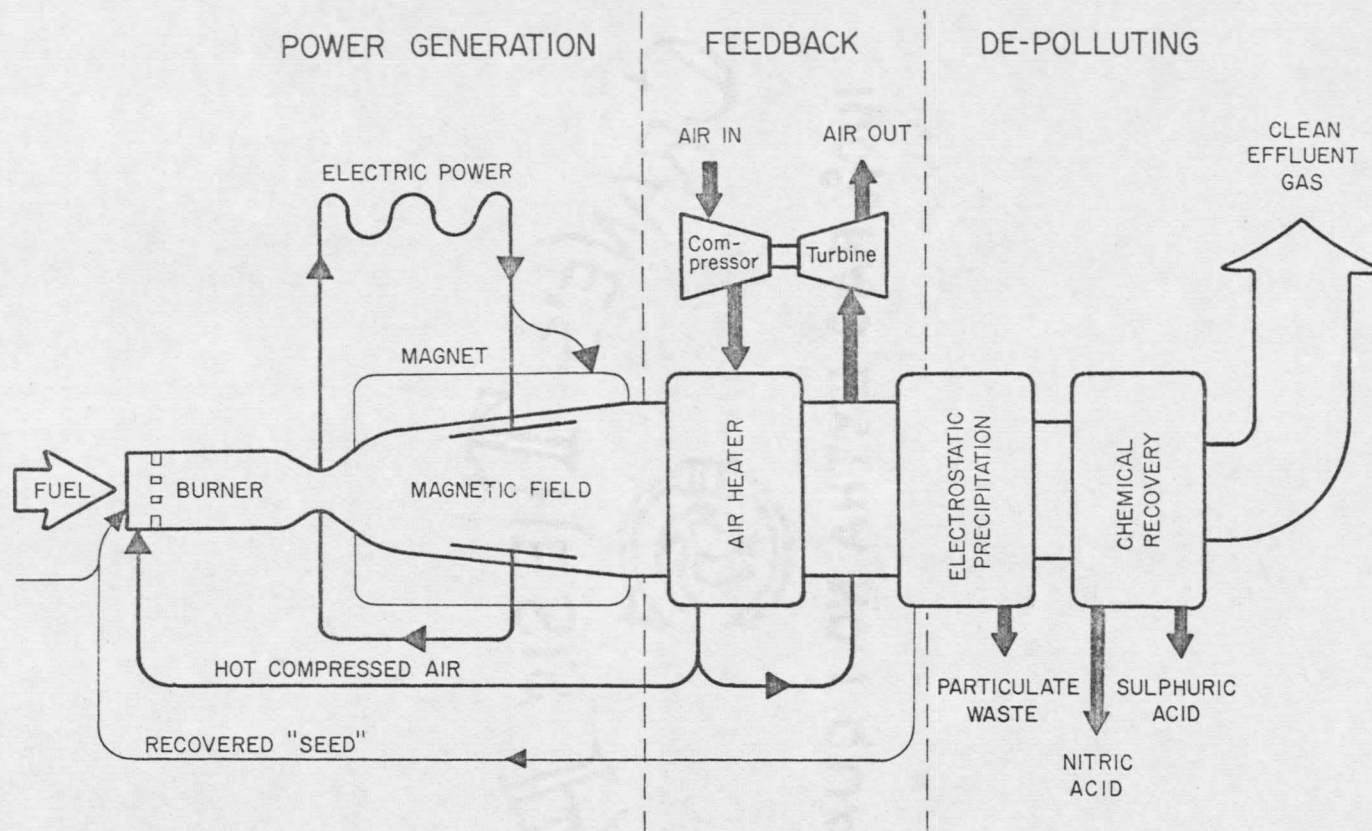


Figure 2. Basic Flow Diagram of the Magnetohydrodynamic Electrical Generating System. (19)

produce an electric current. In the MHD system an electrical conducting plasma is passed through a generator at super-sonic speeds. Around the generator is a superconducting magnet to supply the magnetic field. Thus, by the movement of the conducting plasma through the magnetic field, an electric current is produced. MHD is more efficient in that the steam turbine and generator are eliminated.

The plasma is produced by burning fuel with compressed, preheated air (or oxygen) and a seed containing potassium is added to increase the plasma's electrical conductivity. But the potassium must be recovered by electrostatic precipitators in order to make the process economical. This sort of electrical generation has an efficiency of about 60% as compared to about 40% with steam generating systems.

Coal is the most likely fuel to be used in the MHD process because of its great abundance, but it does present problems. The biggest objection is that the ash in the coal is very erosive to the generator at high temperatures, and it interferes with potassium recovery. Therefore a cleaner fuel needs to be proposed for electrical generation by MHD.

Methane and oil are clean fuels, but they contain a considerable amount of hydrogen which has poor electrical conductivity. What is needed then is a fuel free of ash and low in hydrogen content.

The problem with the use of coal is that present processes are found to be uneconomical. New, unique technological advances will be required to help solve the United States' energy demands and to help utilize Montana's coal resources. The industrial development for the state of Montana based on coal will give the state an economic base that will help to alleviate the frustrating economic situation that the state now faces.

C. Coal Structure and Composition

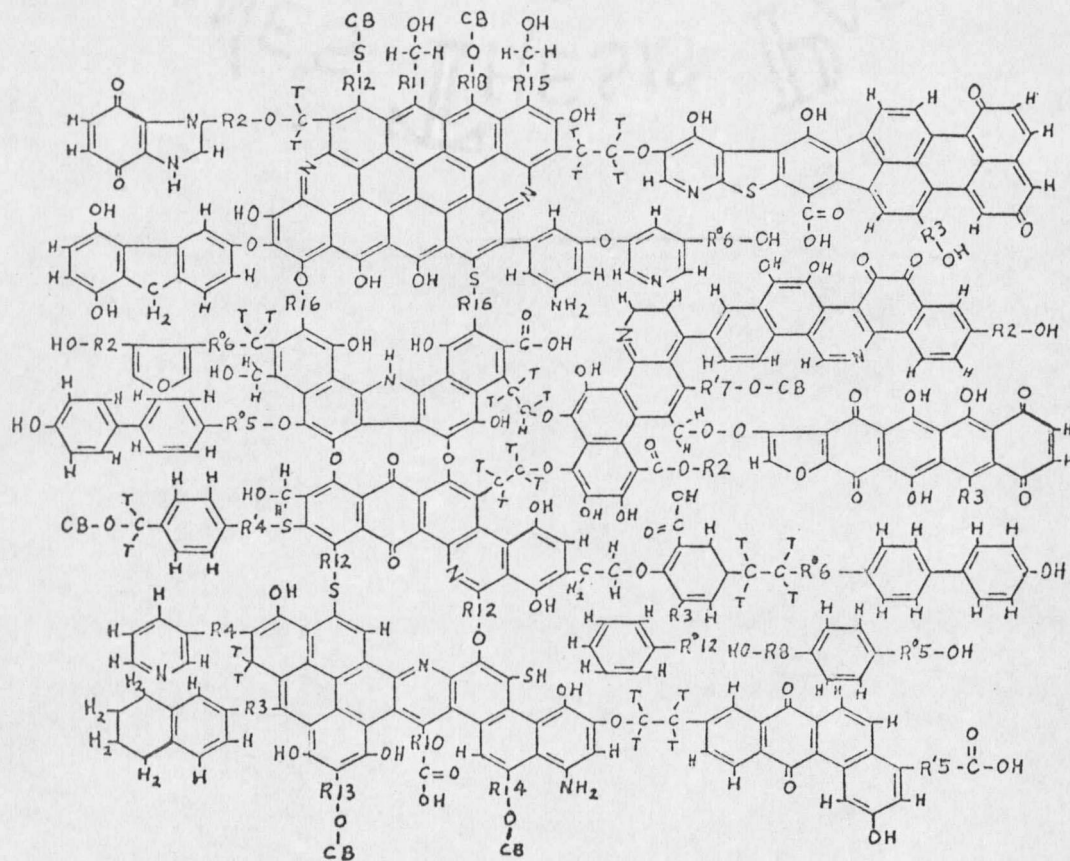
Coal in itself is not a chemical, but rather it is a mixture that is found to be non-uniform and very complex. One of the analyses of coal is called the proximate analysis which breaks coal down to water, volatile matter, fixed carbon, and ash. The volatile matter is that material which will vaporize when heated to a high temperature (900°C), excluding water. The remaining organic matter after heating is called fixed carbon, and the inorganic matter is called ash.

The coal can be further broken down by means of the use of the ultimate analysis. This determines the amount of carbon, hydrogen, sulfur, nitrogen, and by difference, oxygen in the organic portion of the coal.

The structure of coal is really not very well known, particularly for the lower grade coals such as sub-bituminous and lignite. However, in order to get some sort of an idea of the complex structure we are working with, a typical structure of a high volatile coal is shown in Figure 3.

The arrangement of ash in coal is very complex and is not fully understood. However, the elements in the ash are known; it contains silicon, aluminum, iron, titanium, phosphorus, calcium, magnesium, sodium, potassium, sulfur, and many other trace elements including uranium.

In order to make chemicals, synthetic crude oil, gasoline, or natural gas, the ash along with the oxygen, sulfur, and nitrogen must be removed. At the same time, the huge structure of coal must be broken down into smaller fragments and hydrogen added to these fragments.



- R°N Alicyclic Rings of N Carbons
- RN Alkyl Side Chains of N Carbons
- R'N Unsaturated Alkyl Chains
- CB Cross-bonding to Other Heterocyclic Groups
- T Tetrahedral Bonds

Figure 3. Typical Cross-bonded Structure for High Volatile Coal. (20)

II.. HISTORICAL BACKGROUND

A. Coal Liquefaction Through 1960

In order to understand why this research project took the direction that it did take, it would be most helpful to understand the historical background of coal conversion. Our primary concern is coal liquefaction, so this topic will be discussed in some detail.

The first successful attempt to convert coal to an oil was achieved by Charles Berthelot in the 1860's. He reacted the coal with hydrogen iodide in a sealed glass tube at 270°C for 24 hours (21). Under these conditions, his method was far from being an acceptable commercial process and remained a laboratory curiosity until 1910. At this time Germany became concerned about shortages which were developing in their high grade coals, and they asked Bergius to investigate the production of coal from peat. During the course of these experiments, he reacted his coal product from the peat through the use of hydrogen in a high pressure autoclave (2,000 psi) at a fairly high temperature (450°C) to form an oil. In 1913 he applied for a patent for the production of oil from coal, and as a result he received a Nobel prize.

After the First World War, I. G. Farben (a German dye trust) obtained the Bergius patents and developed the process to the point that it was technically feasible to make oil from coal. I. G. Farben joined with Standard Oil of New Jersey, Royal Dutch-Shell Co., and the British Imperial Chemical Industries to form the International Hydrogenation Patents Ltd. The process that they had licensed was called the Bergius process. This process is shown in Figure 4.

The Bergius process has been the standard method of coal hydrogenation and in recent years many modifications of the process have been made in order to make it more economical. Because of its importance, the process will be discussed in some detail.

There are two basic steps in the Bergius process; the first step is the liquid-phase hydrogenation and the second step is the vapor-phase hydrogenation. In the liquid-phase, coal is processed mostly to a middle fraction oil which boils below 325°C . This oil is then sent to the vapor-phase hydrogenation unit where it is processed to gasoline and aviation fuel.

In the liquid-phase hydrogenation, coal and a catalyst (which increases conversion of coal to oil) are

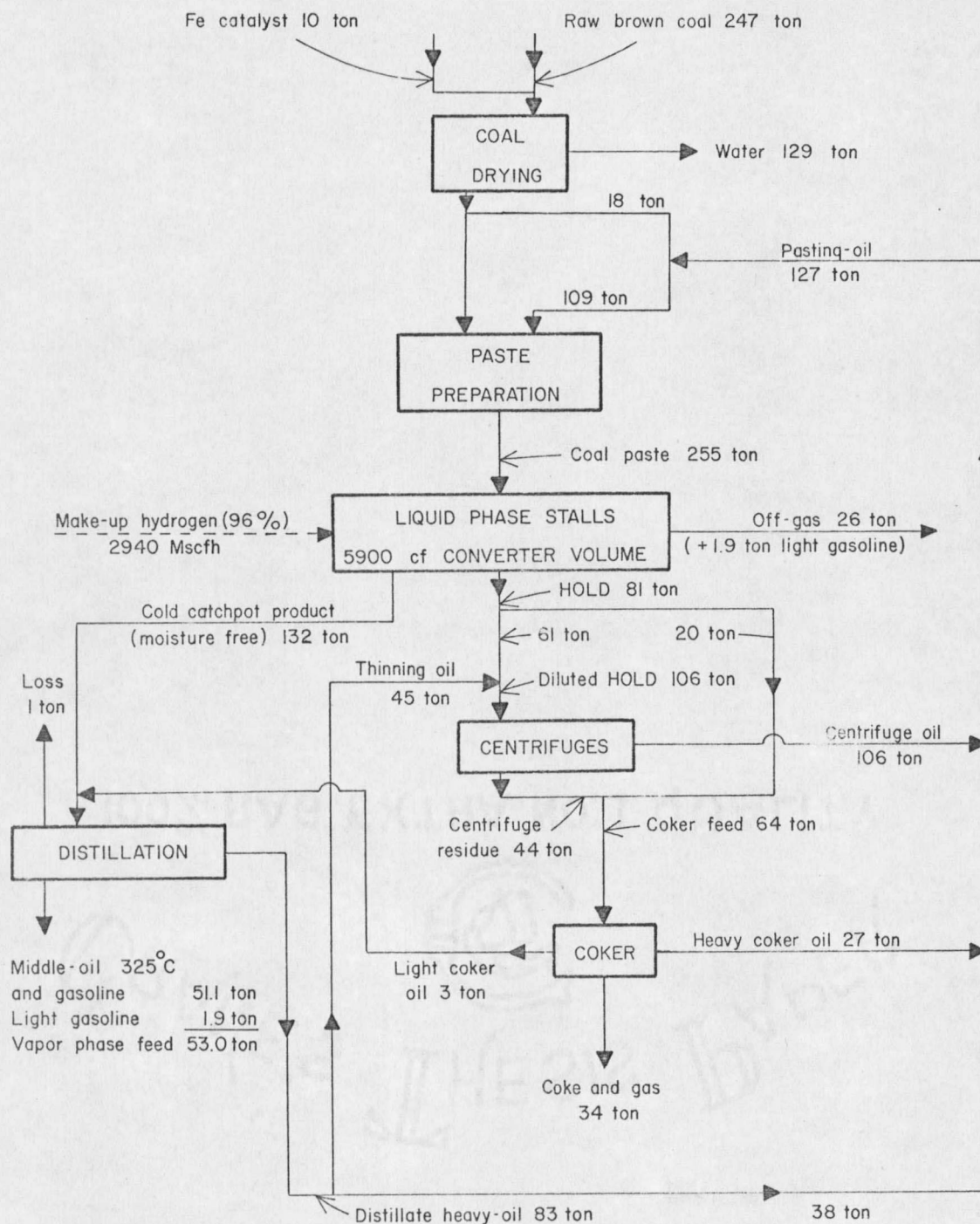


Figure 4. Liquid-phase Hydrogenation in the Bergius Process. (22)

added to a pasting oil, which forms a slurry. A slurry is used because it can easily be transported to the reactor, and conversion is increased if the coal is in an oil medium.

The slurry passes into a converter where it is contacted with hydrogen for one hour at 450°C and 10,000 psi. After the reaction, a considerable amount of light oil and gas pass out of the reactor. The light oil is then condensed and saved for the vapor phase hydrogenation. The liquids and solids are passed through centrifuges to separate the unreacted coal from the heavy oil. Most of this heavy oil is used as the pasting oil and the centrifuge residue is sent to the coker. There, coke is produced, which prevents the pasting oil and the coal slurry from becoming too viscous to be pumped.

The hydrogen is supplied by reacting coal and water to form hydrogen and carbon monoxide. The carbon monoxide is then reacted with water to form more hydrogen and carbon dioxide, with the latter being removed.

The product from the liquid-phase, middle oil, goes to the vapor-phase hydrogenation system which consists of a high pressure hydrogenation reactor with a fixed bed of an expensive catalyst (nickel, tungsten). The primary

products after this treatment are gasoline and aviation fuel.

During World War II, Germany had twelve such coal hydrogenation plants (most of which had minor modifications) which supplied fuel for the German Air Force and Army. The plants were not very large and all twelve plants combined produced only 100,000 bbl/day of liquid hydrocarbon products. A single large United States refinery today will easily produce an equivalent amount of oil products.

After the war, a great deal of interest in coal liquefaction developed. Russia (which has about one-half of the world's known coal reserves) moved many of the German plants to Siberia for research in coal conversion (23). England used its large Bergius process industry to manufacture oil and in this way cut down on oil imports; and in the United States, the Bergius process was demonstrated by the United States Bureau of Mines using American coals (24,25). Most of the information used to build the demonstration plant was captured from the Germans.

The Union Carbide Corporation used the Bergius process for several years to obtain chemicals from coal. However, after 1953 there was not a single Bergius plant

in operation. The reason for this was that the oil and gas companies were easily meeting demands by conventional methods of production and by importation. The other factors resulting in the decline of the Bergius process were economic in nature.

There are several reasons for the economic failure of the Bergius process. Perhaps the biggest obstacle was the high pressure of 10,000 psi and the long residence time that were required in the process. This required a large amount of steel, large compressors and pumps, which in turn meant a large capital investment. In the 1940's, 18 tons of steel and 13,000 dollars of investment per barrel of gasoline per day were required in the process. To make gasoline from coal using the Bergius process, it cost 22.6 cents/gallon, whereas gasoline from an oil refinery would cost about 6 cents/gallon (21). The other serious set-back is the cost for the production of the hydrogen. In some cases this can account for one-third of the cost of the entire plant.

Other minor obstacles included pump failures due to the abrasiveness of the coal slurry; this is particularly serious to high pressure pumps. The other mechanical problem was that the oil could not easily be separated

from the solids in the centrifuges.

By using only the liquid-phase hydrogenation in the Bergius process and milder conditions, a tar could be produced. This is what the Germans did in order to form an essentially ash free product which could be used to produce electrode carbon for their aluminum process. This modification of the Bergius process became known as the Pott-Broche process, and had very little significant importance after World War II (26).

At the same time that the Bergius process was being developed, Germans by the names of Fischer and Tropsch developed the process of using carbon monoxide and hydrogen to make oil, where the CO and H₂ are reacted at 250°C by using nickel, cobalt, and iron as catalysts. The synthetic crude oil produced was not of very good quality; however, the synthetic Diesel fuels and lube oils were satisfactory. The Fischer-Tropsch process ran into the same financial trouble as the Bergius process had, but presently there is still a Fischer-Tropsch plant in South Africa.

Between 1953 and 1960 there was really very little interest in coal conversion with the exception of the interest shown by the United States Bureau of Mines which

tried to make improvements in the Bergius and Fischer-Tropsch processes. For the Bergius process they tried to find more active catalysts for the liquid-phase hydrogenation in order to decrease the pressure requirements of the reaction. This was done, but the catalysts were very expensive and would have had to have been recovered from the products after completion of the reaction.

B. Coal Liquefaction from 1960 - 1970

Because of the predicted decrease in United States oil and gas reserves, the oil companies were stimulated to reinvestigate the coal conversion processes. The Office of Coal Research was formed within the Department of Interior in order to provide funds for the improvement of processes utilizing coal. As a result of this, funds were appropriated for major modifications of the Bergius process in order to make synthetic crude oil competitive with crude oil.

There were three major modifications which have been researched and studied economically to at least the pilot plant state. Perhaps the process most foreign to the Bergius process is Project COED (Char, Oil and Energy Development) shown in Figure 5. It is basically a carbon-

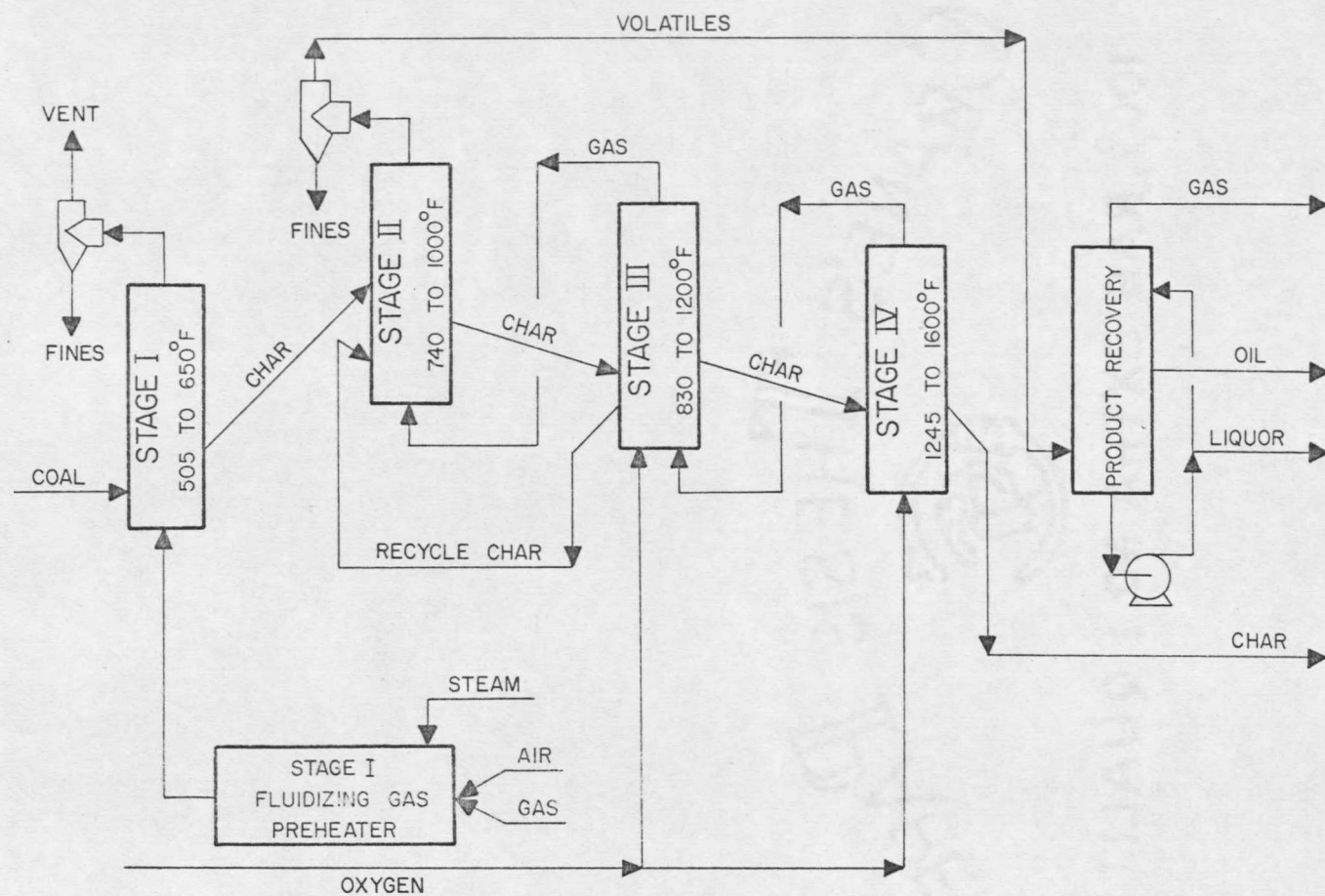


Figure 5. Flow Diagram of FMC's Project COED. (26)

ization process which drives off all volatile matter in multi-stage beds with hydrogen gases going in counter-current flow to the coal and char. The three products that are formed in this process are: gas, a high grade synthetic crude, and char for boiler feed (27). Conversion to gas and oil is not very high, but it does eliminate a great deal of the high pressure equipment needed in the Bergius process. A large amount of char is produced and char is generally considered to be an undesirable product.

H-Coal (Figure 6) is a single stage process using an ebulated bed of a very expensive, reactive catalyst (28). This process can be operated at 2,500 psi to obtain 90% conversion to an oily product and 70% yield to a middle oil which could be used as a refinery feed stock. The reduction of reactor operating pressure plus the simplification of the process resulting in a reduction of plant capital investment, are important factors which makes this process quite attractive.

The process receiving the greatest financial support is the Consol Process (Figure 7) developed by Consolidation Coal Company. This process yields a 70% conversion of coal to a synthetic crude oil with the remaining being a char by-product. In the first step, oil from the second

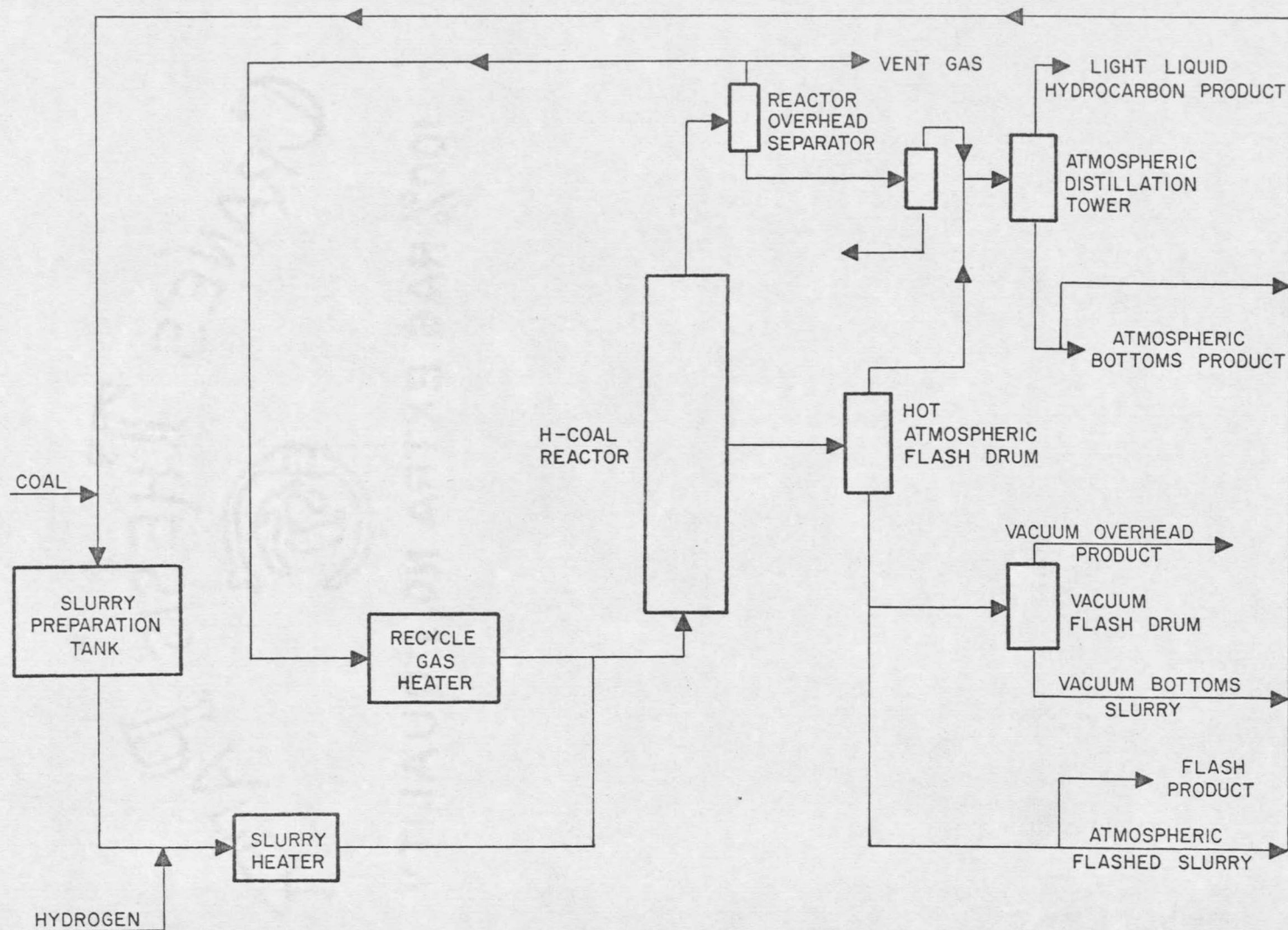


Figure 6. Flow Diagram of Hydrocarbon Research's H-Coal Project. (27)

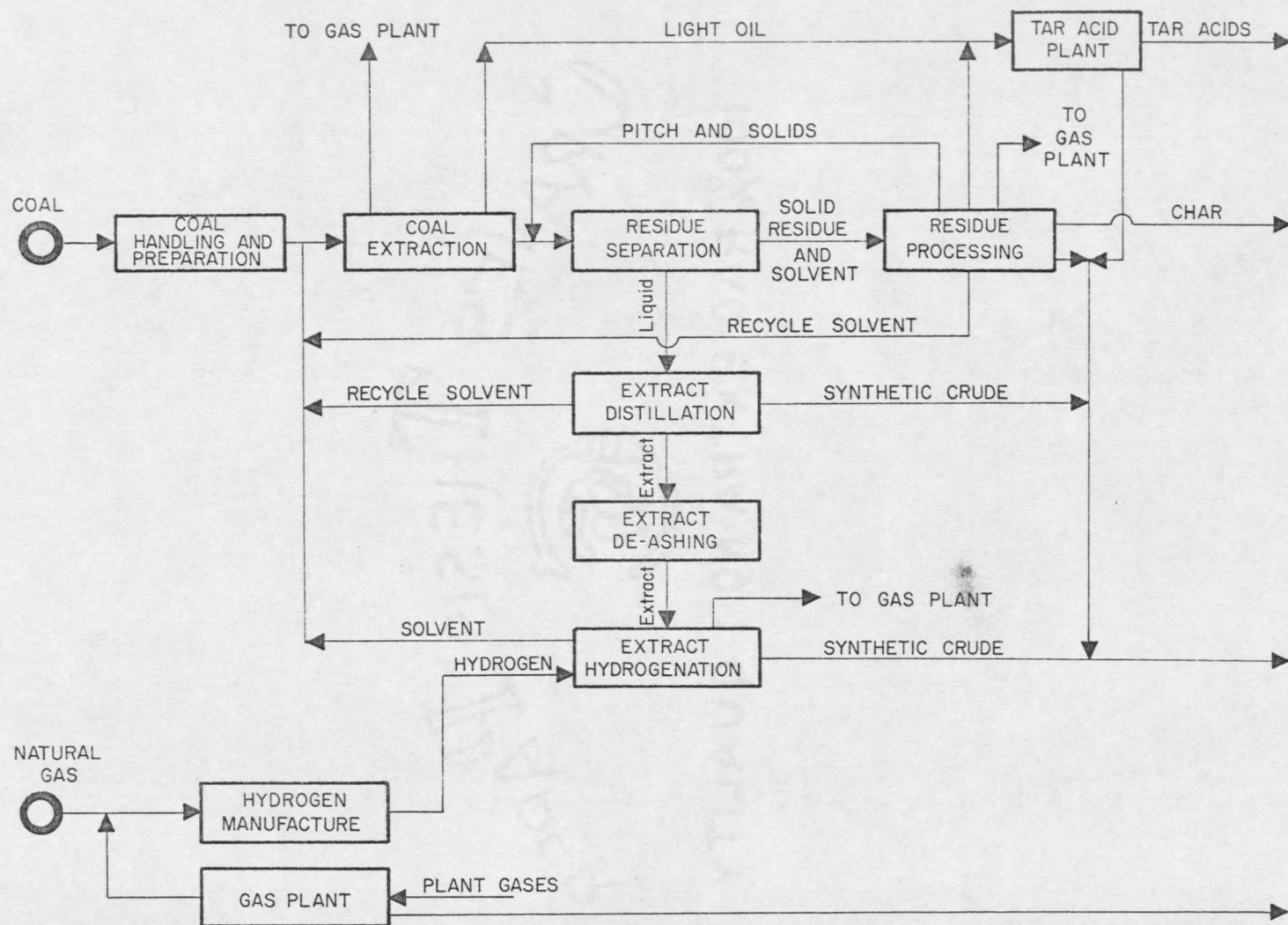


Figure 7. Flow Diagram of Consolidation Coal's Consol Process. (29)

stage is added to the coal and hydrogenation takes place at low pressure and fairly high temperature by means of hydrogen transfer from the second-stage oil to the coal. The heavy oil product is recovered from the first stage by cyclones (the pilot plant is having difficulty with this particular step) and then is passed through high pressure fixed bed reactors with catalysts to produce a high quality synthetic crude and the recycle oil.

Project H-Coal and the Consol Process have improved the state-of-the-art to the point that the cost of synthetic crude oil is approaching the cost of conventional crude oil, but because of the high capital costs, no company would want to take the risk of producing crude oil from coal.

The other major objections to the new concepts include the high cost of the hydrogen and the production of undesirable char. The improvements that were made, however, include the reduction of pressure by means of new catalyst methods and simplifications in the Bergius process.

During this time period, slight modifications of the Pott-Broche process which resulted in the production of a low sulfur and ash product for use in making electrode carbon and for use in steam generating plants, were made

by the Pittsburg and Midway Coal Company.

C. Future Potential Processes

Further research of new processes will certainly be of additional value and hasten the day when hydrogenated coal products will be produced. New concepts are being investigated, and an article written by G. Alex Mills, which this author considers to be a classic in coal liquefaction, describes new concepts which may produce a new generation of coal conversion processes (30). A very brief description of each of these new concepts will be given.

Complexes of transition metals used as hydrogenation catalysts have been studied by the Bureau of Mines. The results show selectivity and activity at a relatively low temperature (200°C).

Massive amounts of halide catalysts, developed by Consolidation Coal provides the promise of production of a light oil from coal in only one step. However, "a commercial process using metal halide catalysts must provide a viable method for regeneration of the catalyst (30)." The Chemical Engineering Department at Montana State University is working to solve the regeneration problem.

Organic hydrogen donor solvents have been studied

for years and with future investigation it is possible that a satisfactory solvent will be found. Also, alkali metals are being explored through the use of several different methods. The Bureau of Mines is using alkali metals as a hydrogen activation catalyst, reduction by alkali metal amines, and electrochemical reduction of coal. Reductive alkylation is another method being investigated.

D. Water-Gas Shift Reaction on Coal

The other process which Mills supported as giving considerable promise as a new generation process was the use of the water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \longrightarrow \text{H}_2 + \text{CO}_2$) with coal. Rather than adding hydrogen to the reactor, carbon monoxide and water were added with the shift reaction taking place, thus producing the hydrogen. Since the hydrogen is produced in situ, it is available to the coal in a nascent form. Hence, it is much more reactive than gaseous hydrogen and gives greater conversion in a shorter period of time than does the molecular hydrogen.

The first time that this reaction was used on coal was in 1921 by Fischer, who noted that the shift reaction on coal liquefied more of the coal than gaseous hydrogen liquefied (31). More work was done during the early

1920's, which showed that it did work well on coal but experimentation still did not succeed in hydrogenating asphalt (32,33). "Although the early results looked promising, the relatively low conversions, the emphasis on a one-step process for converting coal to gasoline, and the impact of the Fischer-Tropsch reaction caused the carbon monoxide plus water approach to be ignored after 1925 (34)."

The reaction with coal was not investigated again until about 1968 when the United States Bureau of Mines decided to reinvestigate the reaction. Because of the reaction's increased conversion over that which used gaseous hydrogen and because of the advent of new hydrocracking catalysts which would convert the coal product of the shift reaction to gasoline, the study was instigated by the Bureau of Mines.

Several runs were made using carbon monoxide and water with bituminous coal and Noonan, North Dakota lignite using alpha-naphthol and phenanthrene as solvents. The most striking curve that they obtained is shown in Figure 8. This figure illustrated the comparison of the conversion of coal to a benzene soluble material when CO and H₂O are used in the reactor and when hydrogen alone

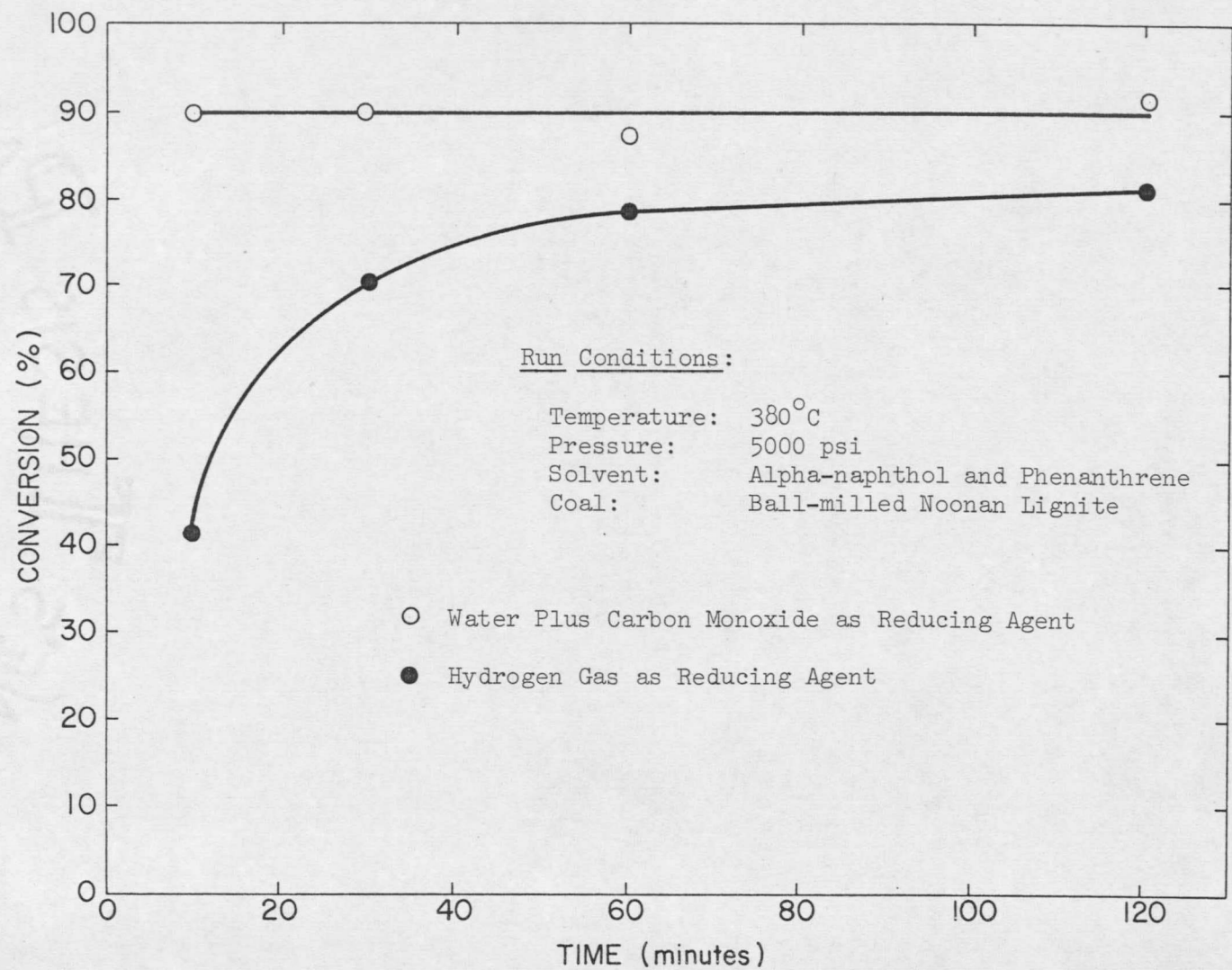


Figure 8. Coal Conversion Results Obtained by The United States Bureau of Mines. (34)

was used in the reactor.. When CO and H_2O are used the conversions took place in a much shorter time and the conversion was much greater than when hydrogen was used. Thus, high conversion was achieved in a short time without the aid of catalysts.. Another paper emanating from the Bureau's work (35) was published later (this is not found in the literature).. In this paper, Appell and Wender discussed hydrogenation of different materials by using CO and H_2O .. They were trying to understand why the reaction works on coal. They then postulated some possible mechanisms.. The conclusions that they reached were: 1) that the reaction is effective because of the hydrogenation with activated hydrogen produced by the water-gas shift reaction, 2) that the introduction of alkyl groups in the coal aids the reaction, and 3) that carbon monoxide has a unique ability to cleave certain types of bonds, or to inhibit condensation reactions leading to benzene-insoluble materials. At the time that this investigation was instigated at Montana State University, that was all the information about the shift reaction on coal that could be obtained. No literature has been published since that time.

The results of this work, particularly Figure 8,

prompted us to investigate processes which could use this reaction, thereby, hopefully reducing the cost of coal hydrogenation. Before a plant could be designed and economically evaluated, experimental runs had to be made on various types of coal in the Fort Union region using several different conditions to see how well they reacted and to see what characteristics the products would possess.

III. RESEARCH OBJECTIVES

The primary objective of this project was to develop a coal liquefaction process which would: 1) help relieve present and future energy problems of the United States, 2) incorporate the water-gas shift reaction because of its rapid reaction and because of its elimination of a catalyst, by-product char and of gaseous hydrogen production in the process, 3) utilize the coal in the Fort Union formation, particularly the sub-bituminous coal and lignite of Montana, and 4) be economically attractive.

Supporting research had to be conducted in order to meet the primary objective. Various types of coal were reacted using several different conditions in order to obtain data for a plant design. Also, the quality and quantity of the gas, liquid, and solid products produced by the reaction had to be investigated. The properties of the hydrogenated product had to be studied to determine its uses, or the need for further processing which would result in the production of a usable product.

It was also hoped that additional information could be obtained which would give a clue as to why or how the shift reaction hydrogenated coal much more effectively.

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than did the process which used gaseous hydrogen.

IV. MATERIALS, EQUIPMENT, AND PROCEDURE

A. Materials and Analysis of Materials

Four coals were used in the experimental runs. Sub-bituminous coal, which was originally mined near Colstrip, Montana, was obtained from the steam-generating plant in Billings. The sub-bituminous coal could be obtained in either pulverized form (minus 200 mesh), or in crushed form (minus one inch). The other coals were lignites which came from Sidney, Montana (Savage, Montana mine), Noonan, North Dakota, and Stanton, North Dakota. Of the lignites, only Savage lignite could be obtained in a pulverized form. The ultimate, proximate, and ash analyses for each of the coals are given in Table I.

The pulverized coal had lost a considerable amount of water since it was transported with hot air in the steam-generating plants, but the coal was kept enclosed in metal drums to prevent further aging (water loss and oxidation) by air. The crushed coal was kept in large plastic bags with as much air as possible being forced out of the bags.

The analysis of coal which varied the most even when the coal came from the same mine, was the proximate anal-

TABLE I. Proximate, Ultimate, and Ash Analyses for Colstrip Sub-bituminous and Savage, Noonan and Stanton Lignites.

Coals:	Colstrip Sub-bituminous	Savage Lignite	Stanton Lignite	Noonan Lignite
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Proximate

Moisture	23.9%	37.9%	38.4%	35.4%
Volatile Matter	30.9	25.1		
Fixed Carbon	37.6	29.6		
Ash	7.6	7.4	7.5	6.9

Ultimate

Moisture	23.9%	37.9%	38.4%	35.4%
Carbon	50.3	39.2	38.4	42.2
Hydrogen	3.4	2.6	2.7	2.9
Nitrogen	0.7	0.6	0.5	0.7
Sulfur	0.4	0.5	0.4	0.3
Oxygen	13.7	11.7	12.1	11.6
Ash	7.6	7.4	7.5	6.9

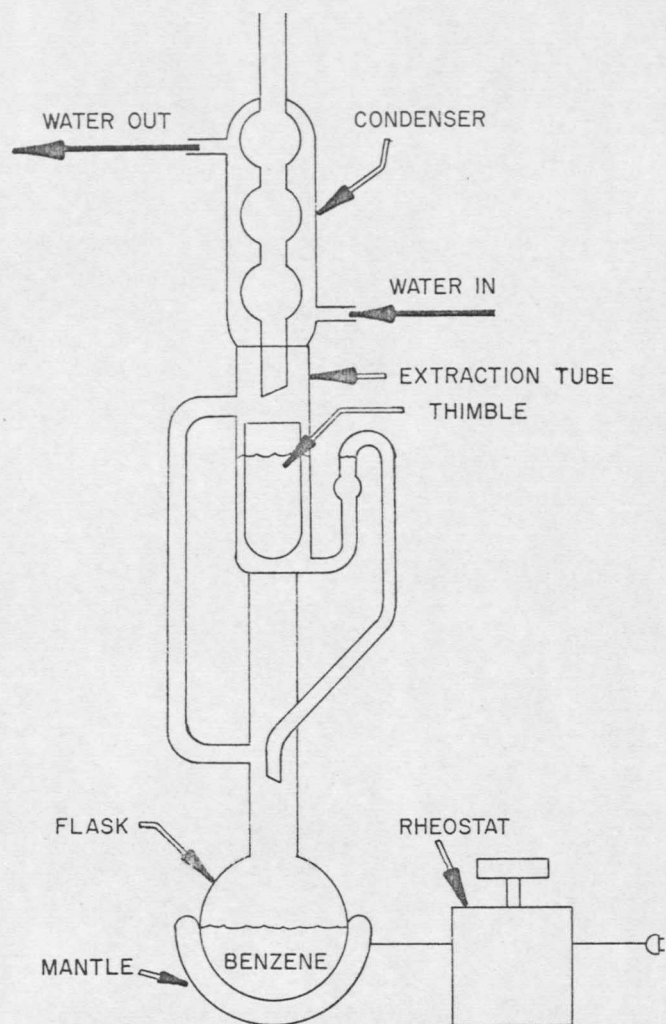
Ash Analysis of Major Components

SiO ₂	36.4%	27.1%	36.0%	30.0%
Al ₂ O ₃	17.6	18.5	14.0	11.0
Fe ₂ O ₃	4.6	5.1	7.2	6.6
TiO ₂	0.4	0.7	0.5	0.6
P ₂ O ₅	0.8	0.2		
CaO	22.7	15.6	18.0	21.0
MgO	9.4	6.6	4.8	4.7
Na ₂ O	0.3	0.2	5.4	11.0
K ₂ O	0.5	0.4	1.3	0.6
SO ₃	14.9	14.6		

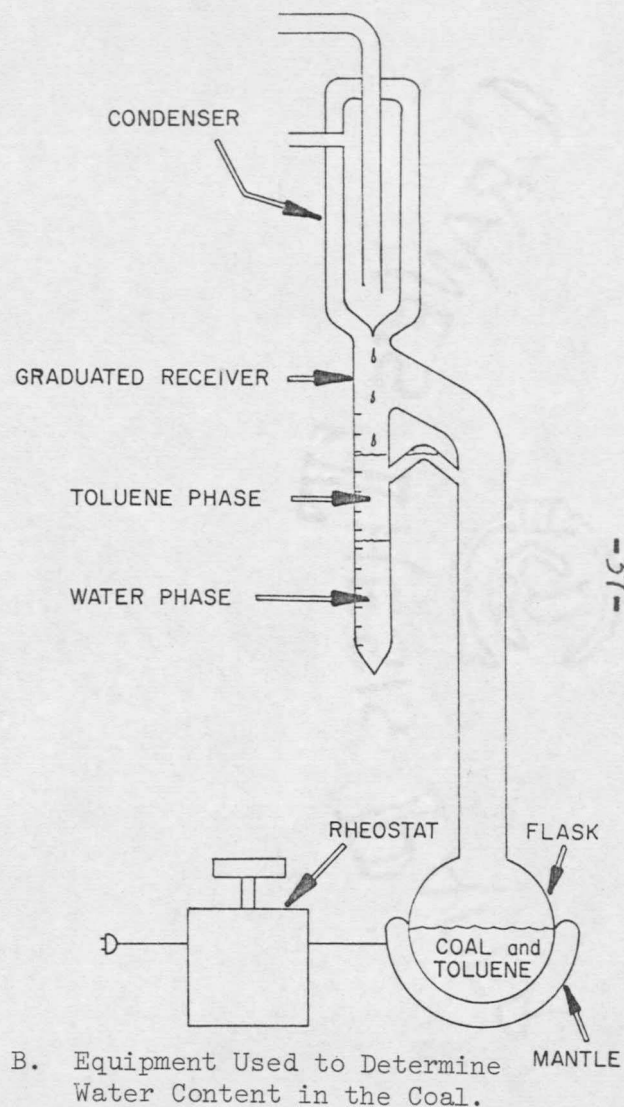
ysis because of the variability of the water and ash contents. The water content was determined by using the apparatus shown in Figure 9B. Toluene and a known amount of coal were added to the boiling flask. The water from the coal and the toluene vaporized; condensed in the condenser, and collected in a graduated receiver with the toluene returning to the boiling flask. The volume of water collected was recorded and a simple ratio calculation was made to determine the percentage of water present in the coal. The ash analysis was made simply by adding a known amount of coal to a covered porcelain crucible. After all of the volatile matter was driven off, the lid on the crucible was removed and the remaining fixed carbon was burned off. The ash was weighed and a calculation was made to determine the percentage of ash present in the coal.

The amount of volatile matter and fixed carbon was not determined since it was of little value to us. The Bureau of Mines in Grand Forks performed ultimate and ash analyses by using standard equipment and procedures (36). Huffman Laboratories in Wheatridge, Colorado did some ultimate analyses using micro techniques on some of the coal hydrogenation products.

The pulverized coal was used as it was received even



A. Soxhlet Extraction Equipment Used to Determine Coal Conversion



B. Equipment Used to Determine Water Content in the Coal.

Figure 9. Glassware and Equipment for Coal Determinations

though it had lost a considerable amount of water (as much as 50%). However, the crushed coal was ground either by using a ball mill or by using a mortar and pestle.

The porcelain line ball mill had about a 15 gallon capacity and steel balls were used. The grinding lasted for about 24 hours, and the coal was then put into closed steel drums for storage. If the coal was ground using the mortar and pestle, about 100 grams was prepared one hour before the run was made. This was done to prevent any aging of the coal caused by extended contact with the air.

In nearly all of the runs a solvent for the coal was used. The solvents tried included alpha-naphthol, phenanthrene, a tar product from a coking process, anthracene oil, and isoquinoline. The tar, which was processed from a bituminous-B coal, was obtained from the United States Bureau of Mines' coking pilot plant in Grand Forks. The anthracene oil was obtained from the Reilly Tar and Chemical Corporation. It is a distillable oil fraction from coking ovens, and has the following composition:

Fluorene	9%
Anthracene	9%
Carbazole	9%
Phenanthrene	35%
Unidentified	38%

The remaining chemicals and solvents such as sodium

carbonate, iron oxide, benzene, toluene, carbon monoxide, and hydrogen were all technical grade.

In a few runs the material being reacted was Esso Bunker C fuel oil and 85/100 penetration asphalt cement. Inspections on these samples are given in Table II, and were determined by Esso Research and Engineering at Linden, New Jersey.

B. Equipment and Procedures for Making Runs

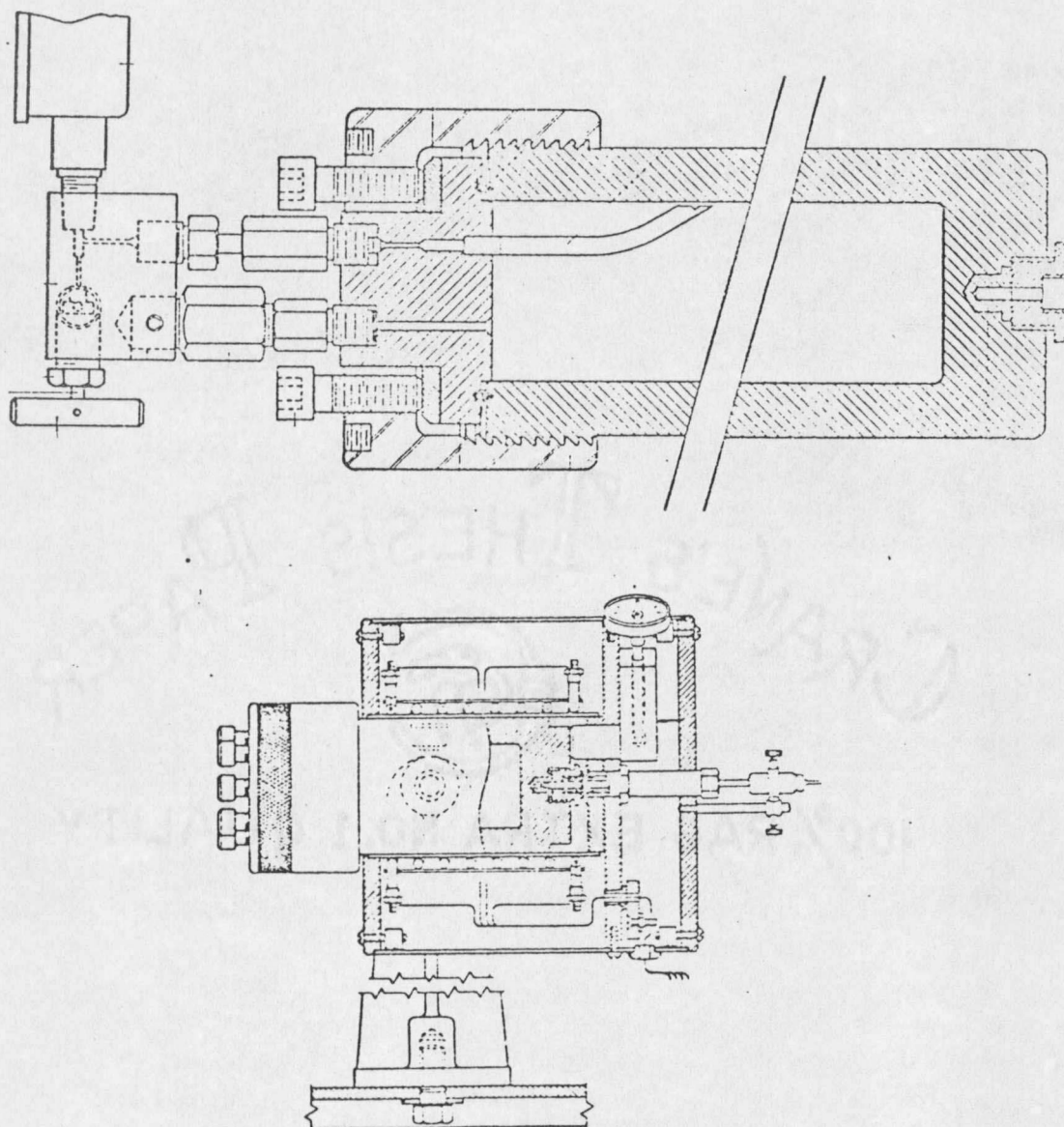
The reactor used for this study was a 500 ml. Parr rocking stainless steel autoclave which rocked at about 36 strokes per minute. It was rated at 400°C and about 8,000 psi at room temperature, although it was frequently run at 450°C. The autoclave and the rocking-heating system are shown in Figure 10.

The pressure was indicated by the pressure gauge on the autoclave valve block; this was periodically checked with other gauges in the system. Temperature was detected by an iron-constantan thermocouple which was placed in the thermocouple well of the autoclave. The temperature was then recorded on a chart recorder. The thermocouple and chart recorder were checked by placing the thermocouple in molten zinc and letting the zinc cool to form a solid.

TABLE II. Inspections on Samples of Bunker C and 85/100 Penetration Asphalt Cement.

<u>Sample</u>	<u>Bunker C</u>	<u>Penetration Asphalt</u>
Viscosity @ 122°F SFS	213	
Viscosity @ 275°F SFS		190
Viscosity @ 140°F, p.		1,800
Penetration @ 77°F		98
Pen. Ratio 39.2°/77°		36
Sp. Gr. @ 60/60°F	0.970	1.015
Flash °F, P.M.	225	500*
BTU/#	18,570	
Ash, %	0.04	
Pour Point, °F	15	
% C	86.1	86.0
H	11.0	10.4
N	0.3	0.5
S	1.9	2.8
O	0.4	0.6*

*Estimated from other data.



Bomb Heater Details

Figure 10. Rocking Autoclave Assembly Diagram. (38)

Because of the latent heat of fusion, the temperature would remain constant for about a minute. This constant temperature was checked with the melting point of zinc at 419°C (39).

Because of FCCO regulations the carbon monoxide was shipped in 1,500 psi cylinders. In order to make maximum use of the CO, a pressurization unit was used to maintain the CO pressure between 1,500 and 3,000 psi. The unit is shown in Figure 11.

The commercial CO cylinders were connected to the system, and some of the CO was added to the high pressure cylinder. Then hydraulic oil was pumped into the high pressure cylinder, and simply by displacement, the CO pressure was increased to the desired pressure. When most of the CO from the cylinder was consumed the oil was drained, more CO was added, and the cycle was repeated.

In order to make a run, the material (which generally consisted of coal, solvent, and water) was weighed to the nearest one one-hundredth of a gram and added to the autoclave. The autoclave was then sealed and placed in the rocker-heater portion of the equipment. The CO was then added from the high pressure cylinder to the autoclave until the desired pressure was reached. The initial

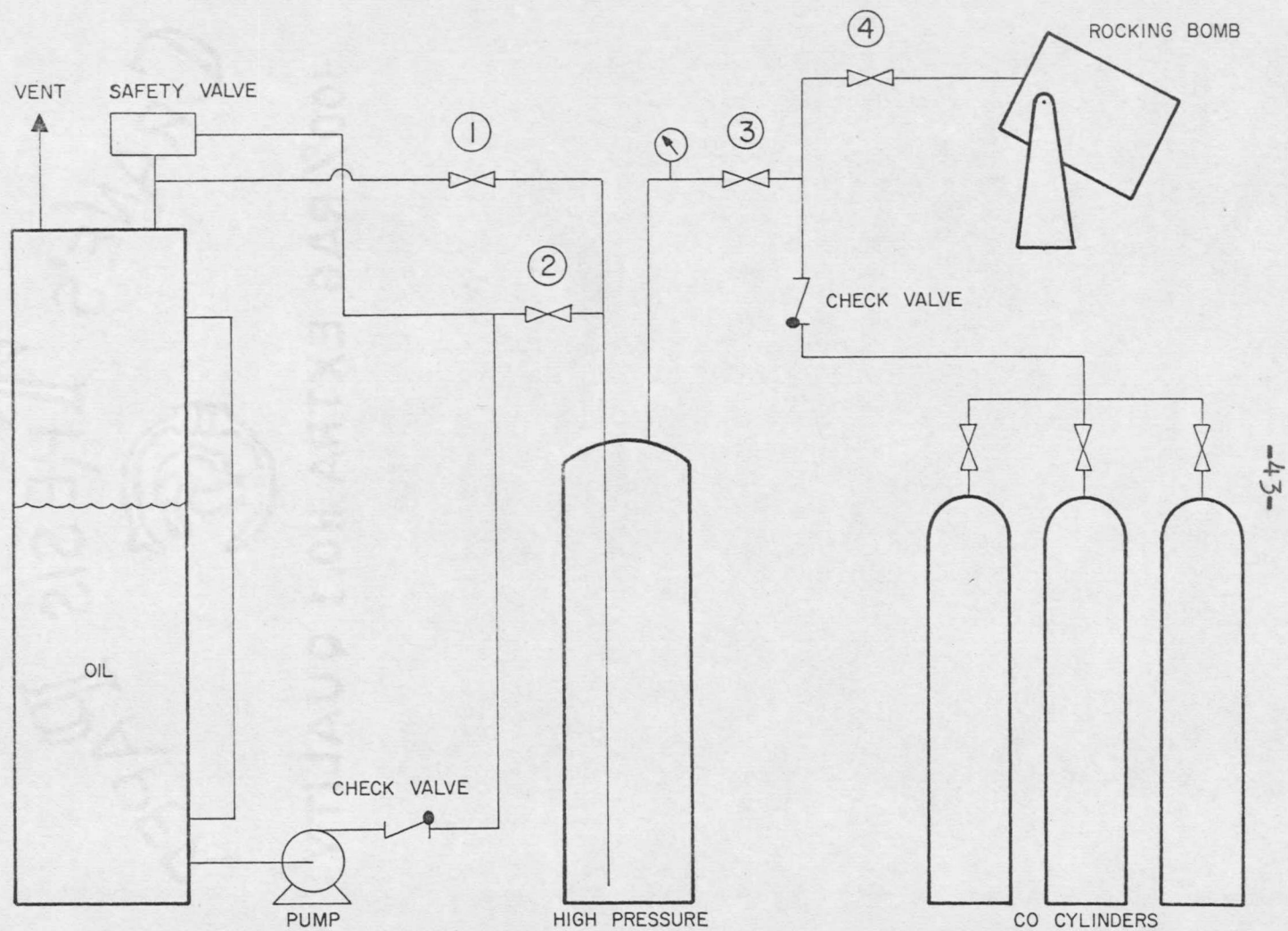


Figure 11. Pressurization Unit Flow Diagram

pressure of most runs was between 1,350 and 1,500 psi.

The equipment was left at static conditions for about ten minutes to check for leaks. As a safety precaution, a Bacharach CO detector was always readily available in case any leak did develop. If there were no leaks, the heaters and rocker were turned on. A typical heating curve for a 15 minute run is shown in Figure 12. It took about 40 to 50 minutes for the autoclave to reach temperature, and once reached, that was considered a reaction time equal to zero. The operating pressure was in the 4,000 to 5000 psi range. After the desired reaction time had passed, the hot autoclave was pulled out of the heaters (by means of threaded pull rods), and set upright on bricks to cool overnight.

C. Reaction Product Analyses

In most of the runs, there were two primary purposes for the analyses. First, the analysis of the reaction gases was made in order to determine the quality and quantity of each constituent. The second, and most important objective, was to determine the conversion of the coal's organic matter to a benzene soluble material. Coal itself is not soluble in benzene, but tar and oil are. Therefore,

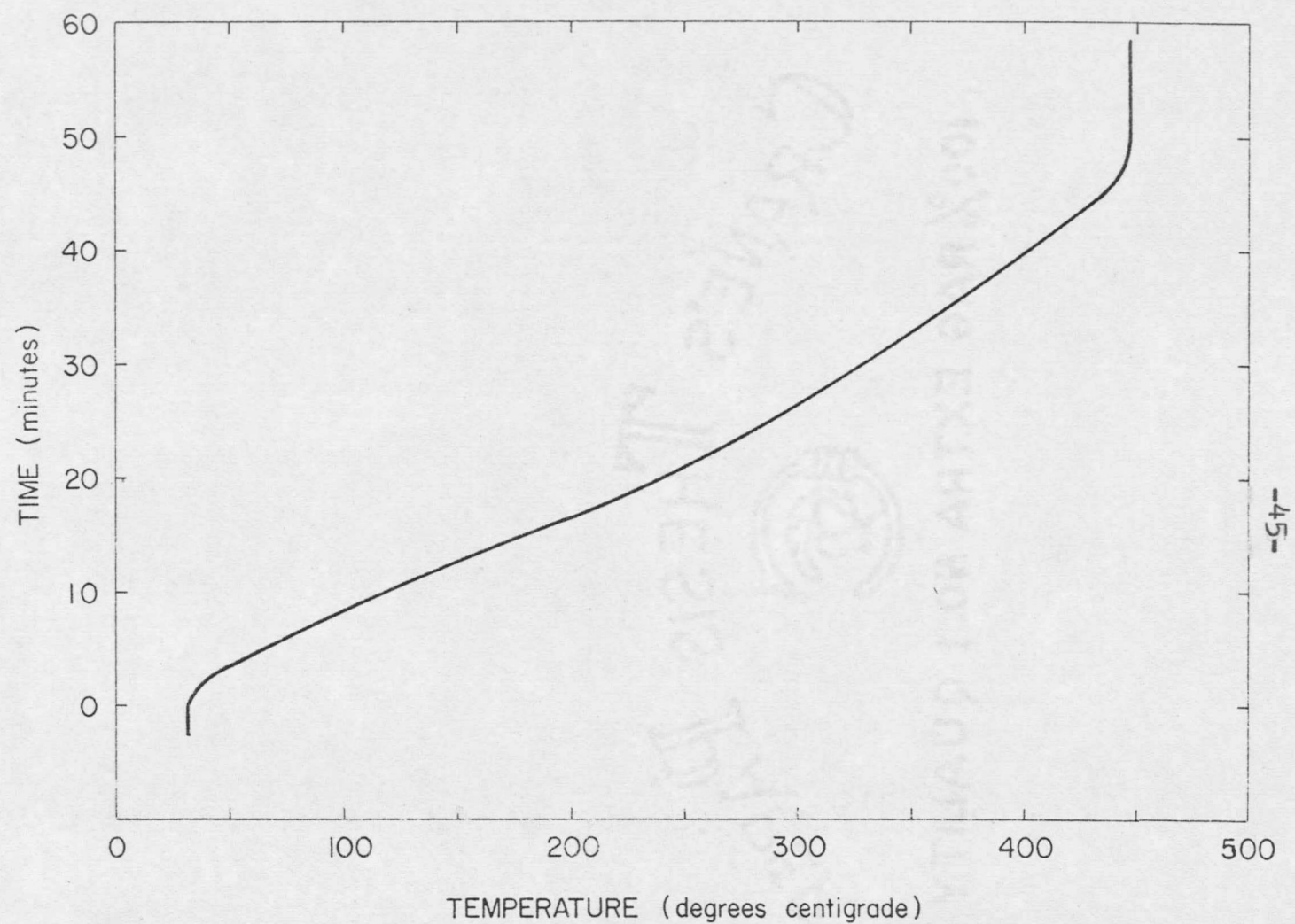
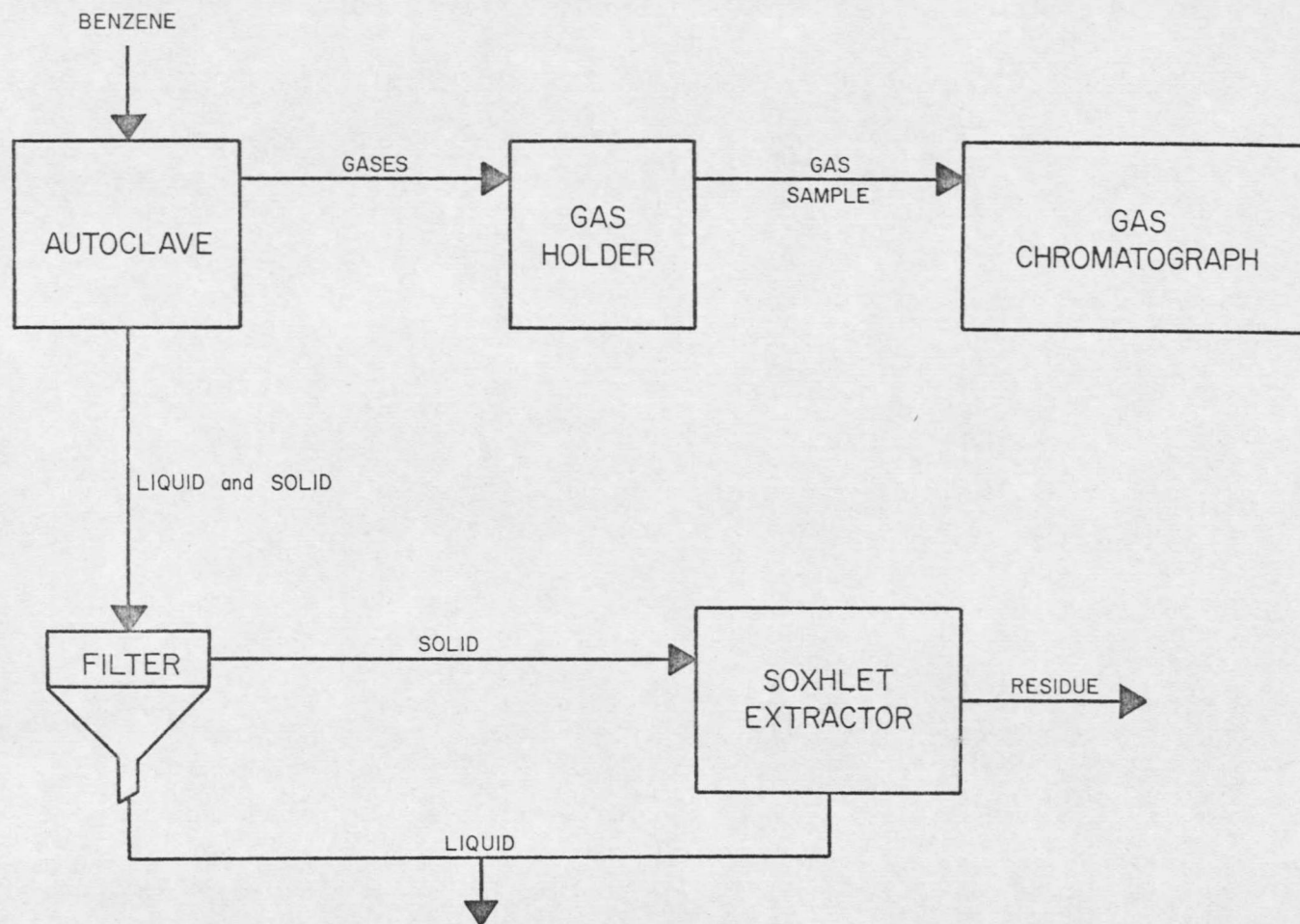


Figure 12. Time Versus Temperature Curve for a Typical 15 Minute Run.

we are able to tell how much of the coal had converted to tar, oil, or gas by this method. Product quality could also be further determined by checking the solubility of the product in hexane. That which is soluble in benzene but not in hexane is defined as asphaltenes, and the material soluble in both benzene and hexane is defined as oil. Hexane solubilities were not made because it turned out that nearly all of the liquid material was hexane insoluble. A block diagram of the analytical procedure is shown in Figure 13.

1. Equipment and procedure for gas analyses:

A 20 gallon drum was equipped with piping and valves so that it could be evacuated; reaction gases were added from the autoclave to the drum, and samples were taken out of the drum through the use of a gas syringe. After the autoclave had cooled overnight the gas was slowly bled (to prevent foaming of liquid) to the 20 gallon drum. Final pressures varied from run to run; because of this, the final pressure in the drum did not always reach atmospheric pressure. As a consequence air was added to achieve the necessary pressure. At the most, 25% of the gas in the drum was air. The drum was then taken to the gas chroma-



-47-

Figure 13. Block Diagram of the Run Analytical Procedures.

tograph to analyze the quantity and quality of the reaction gases.

First a system had to be developed which would detect CO, CO₂, H₂, O₂, N₂, CH₄, C₂H₆, C₃H₈, and C₄H₁₀. In order to make the analysis with the equipment that we had available, the analysis system required two columns in parallel in one gas chromatograph. One column was packed with Porapak Q and the other with a Linde 5A molecular seive. The Porapak Q column (1/4" x 6') detected CO₂ and the hydrocarbon gases while the Linde 5A column (1/4" x 9') detected CO, O₂, and N₂. The oven temperature was maintained at 75°C for both columns and the hydrogen flow rate was 40 cc/min. Since hydrogen was the carrier gas for both columns, the quantity of hydrogen present had to be calculated by difference.

All gas samples were 500 µl, and two standard gases were used, one containing CO, CO₂, and H₂ while the other contained the hydrocarbon gases, hydrogen, and nitrogen. Air was used to standardize the oxygen and nitrogen peaks. Then samples from the reaction gases were injected into the chromatograph. The recorder had an integrator which recorded the area under each peak and gas concentrations were calculated by ratios of the peak area.

2. Equipment and procedure for conversion analyses:

After the gas had been removed, the autoclave was opened, benzene was added and stirred to make a slurry. The slurry was then added to a nine cm. Buchner filter (with a Wattman #2 filter paper) under a vacuum.

The residue remaining in the filter was allowed to air dry for about 12 hours to facilitate easy and clean removal. The residue was then placed in a weighed 100 x 15 mm. double thickness cellulose thimble, and the thimble was then placed in a Soxhlet extraction unit (Figure 9A). The material in the thimble which is soluble in boiling benzene is then removed and added to the boiling flask of benzene. The unit was run for 24 hours or until the benzene was colorless. After extraction, the thimble was removed and placed in a steam heated dryer for 24 hours. The dry thimble and residue were weighed and conversion was calculated.

By knowing the amount of ash and water in the coal, the amount of moisture and ash free (MAF) content of the coal was known. Subtracting the ash from the residue in the dry thimble gave the MAF content of the residue. Then by using the equation:

$$O = \frac{MAF_i - MAF_f}{MAF_i} \times 100\%$$

where O = percent of the organic matter in coal which becomes benzene soluble,

MAF_i = weight of moisture and ash free material in the coal added to the reactor,

MAF_f = weight of moisture and ash free material in the residue remaining in the thimble.

Other analytical procedures were tried in an effort to determine the conversion but this method was by far the most reliable and consistent method.

D. Runs with Special Objectives

Some runs were not done precisely in the manner described above because a special objective had to be met. In some runs sodium carbonate was used as a catalyst in an effort to determine if the sodium carbonate would help to increase the conversion of coal to oil. In these runs, an aqueous sodium carbonate solution was added to coal which had been previously ground by use of the mortar and pestle. After letting the coal air dry overnight, a water analysis had to be performed on that particular sample of coal because that sample of coal would certainly not have the same water content as mined coal. The run was then carried

out in the usual manner.

Several times it was desired to obtain a sample of the hydrogenated product from the coal for analysis. In these runs, no solvent was used to prevent its interference in the product analyses. The product was then placed directly in the Soxhlet extraction thimble. After extraction, the benzene was then distilled (using a hot water bath) from the product. The product was then poured into viles and sent to Huffman Laboratories.

V. RESULTS AND DISCUSSION

A. Results and Discussion of Conversion Analyses

Well over 100 runs were made with the objective of obtaining information which would allow the design of a plant which would utilize the water-gas shift reaction for the reduction of coal. Variables such as solvents, temperature, pressure, type of coal, and time had to be investigated. New ideas were tried in an effort to reduce the capital and operating costs of the potential processes. Also, it was hoped supplemental information could be added about the reduction of coal through the use of the water-gas shift reaction. The easiest and fastest method of making these determinations was by finding out what the conversion of coal to benzene soluble material was. Unless otherwise indicated, 30 grams of coal were used and the water-to-coal ratio for the runs was 0.5.

1. Accuracy of conversion analyses:

The first eight runs were made for two reasons. One was to learn the technique of determining the coal conversion and the other was to determine how much accuracy could be expected from the technique being used. After the first five runs were made, it was felt that a satis-

factory technique had been acquired.. The last three runs were each made under the same conditions and the limits of accuracy were determined to be $\pm 3\%$ on the conversion analyses.

2. Effect of additional water:

Water is already available in the coal; however, it was desired to learn whether additional water would be of any benefit to conversion. Since additional water would increase the operating pressure, a reduction of initial CO pressure had to be made in order to maintain constant operating pressure.

Two sets of runs were made, one set having runs of one hour reaction time using sub-bituminous coal and the other set using Noonan lignite coal with a 15 minute reaction time (Figure 14). From the results, when Colstrip sub-bituminous coal was used, it appears that sufficient water is available in the coal to obtain conversions nearly equal to the conversions obtained when additional water was added. However, for the 15 minute runs on lignite, the additional water does increase conversion significantly.

The reason for these observations seems to be that during the initial part of the runs, the additional water

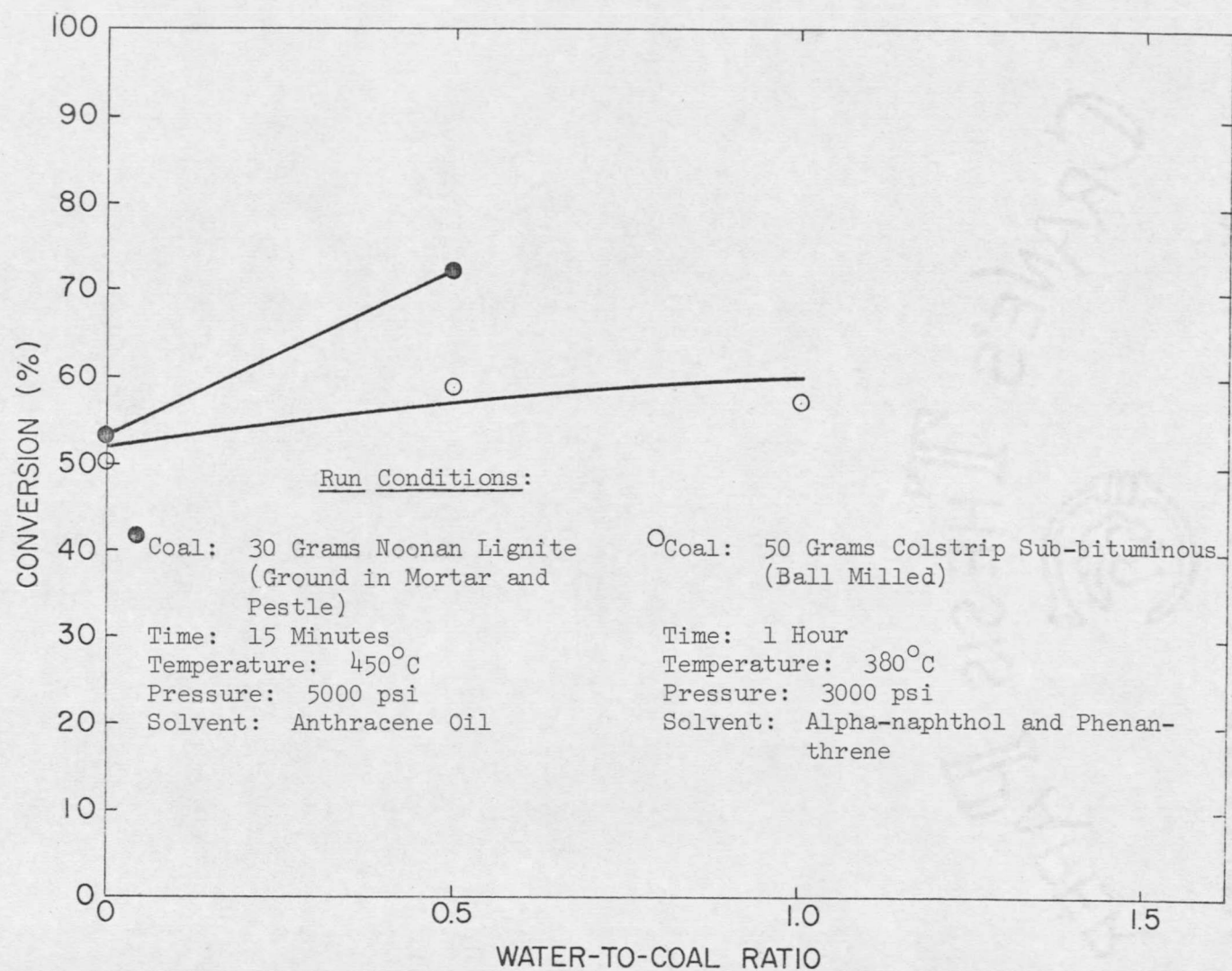


Figure 14. Conversion Versus Water-to-Coal Ratio.

makes more nascent hydrogen available for reaction thereby increasing conversion. But in time (at least in an hour) enough hydrogen is eventually available to reach conversions equal to the conversions found where additional water was added. It is felt that in a continuous reactor where the contact between the gas and the slurry would be much better than in a rocking autoclave, the conversion would be the same with or without the addition of water, even for short time runs.

3. Effect of pressure on conversion:

In a potential coal conversion process it would be desirable to have the operating pressure as low as possible to reduce steel, pump, and compressor costs. The conversion versus operating pressure curve for a ball-milled sub-bituminous coal at two different temperatures is shown in Figure 15. The maximum pressure that was felt to be a safe operating pressure for our equipment was 5,000 psi, especially at 450°C. Pressure was found to have a very significant effect on conversion throughout the pressure range studied.

4. Effect of temperature on conversion:

The effect of temperature on conversion was invest-

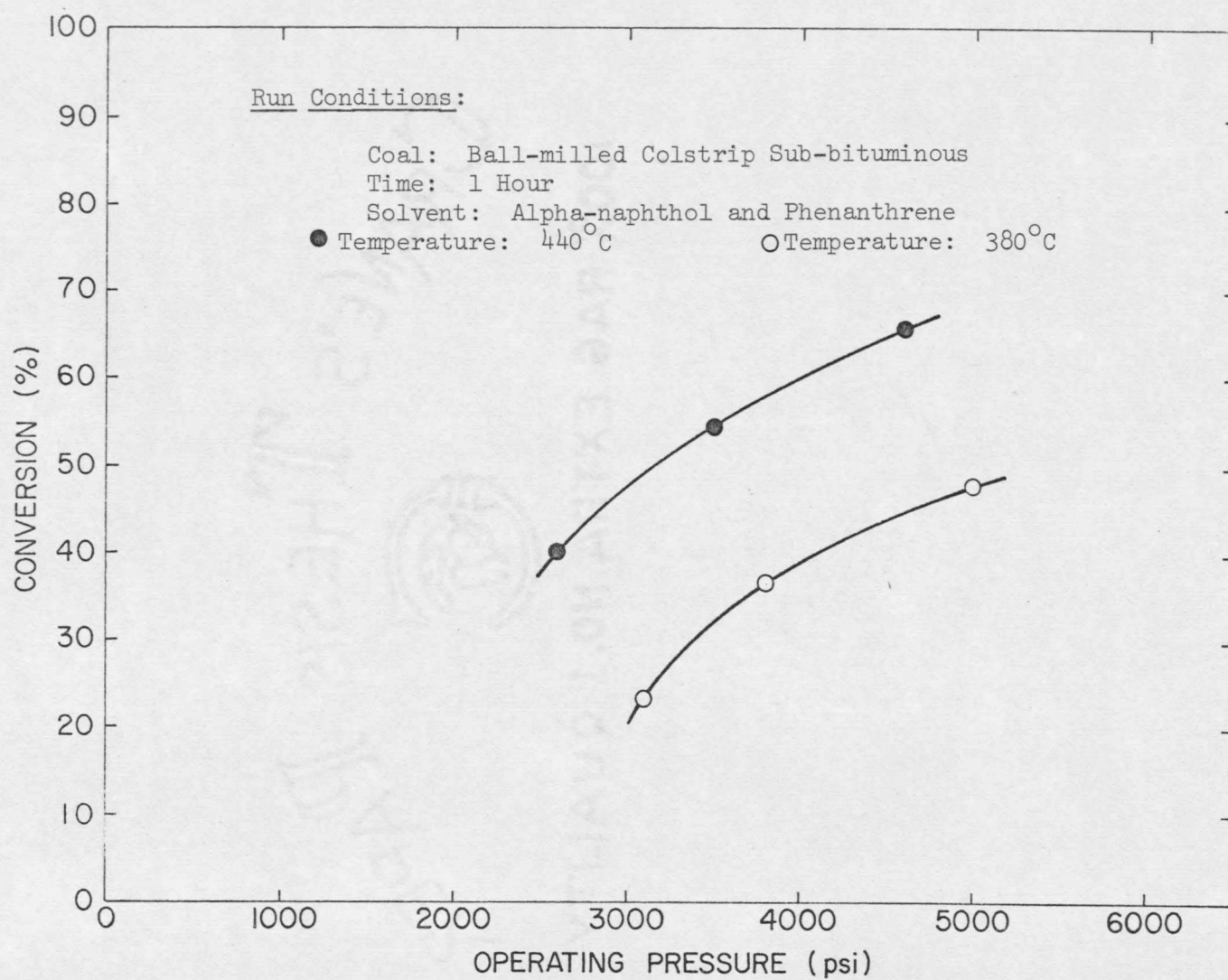


Figure 15. Conversion Versus Operating Pressure for Sub-bituminous.

igated quite extensively and will be shown as a variable in many of the results. Four hundred and fifty degrees Centigrade was the temperature limit of the equipment that was used and below 380°C the conversion was not very significant, especially when the reaction would be increased with increasing temperature (Figure 15).

5. Effect of coal solvents on conversion:

Most of the studies on solvents were done using ground sub-bituminous coal and a few runs were made with ground Noonan lignite. The four solvents studied were: anthracene oil, a 50-50 mixture of alpha-naphthol and phenanthrene (ANP), the tar from a coking process, and isoquinoline.

The best solvent for sub-bituminous coal was isoquinoline and a close second was anthracene oil (Figure 16). The alpha-naphthol - phenanthrene (ANP) mixture was not as good as the first two especially during the short time runs (15 minutes). The tar was by far the most inferior; in fact it was found to be worse than using no solvent at all.

For long time runs (one hour) at low pressure, anthracene oil was always quite superior to ANP, while at

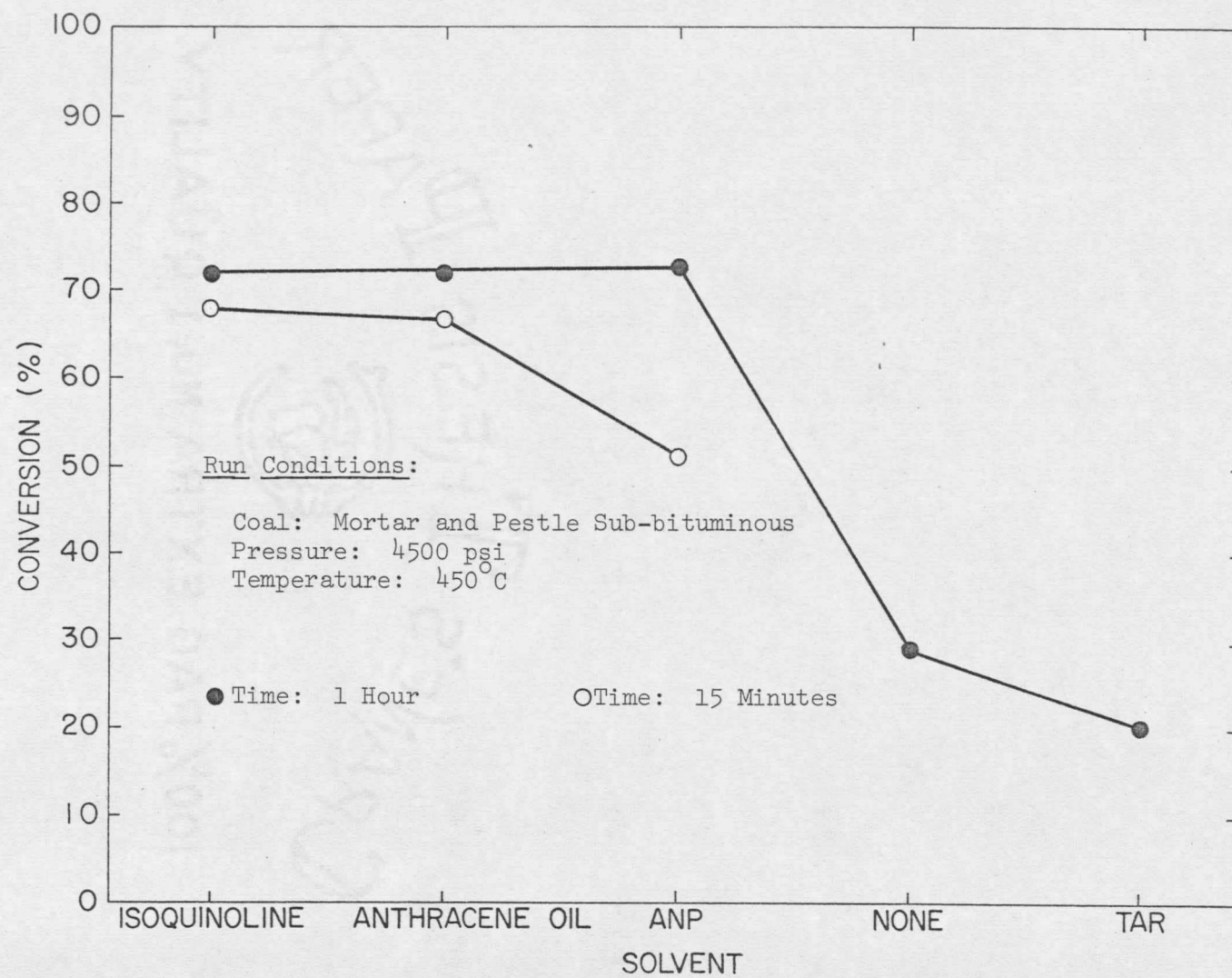


Figure 16. Conversion Versus Type of Solvent with Sub-bituminous.

high pressure the conversion obtained when the two solvents were used were about the same (Figure 17).

When solvent studies were made on Noonan lignite, the results were quite surprising. This time ANP was found to be the superior solvent when it was compared to anthracene oil (Figure 18). About the same conversion level was obtained with isoquinoline as with anthracene oil as solvents which is the same results seen when sub-bituminous coal is used.

Perhaps the reason ANP works better on lignite than it does on sub-bituminous is because alpha-naphthol is a better solvent for the hydrogenated product from lignite. It is noted that lignite has much more oxygen per carbon atom than does sub-bituminous coal (Table I). It is also possible that alpha-naphthol reacts with the lignite's organic structure in some manner, but it does not react with the sub-bituminous coal structure in the same manner. Probably the reason that the tar was such a poor solvent was that some of the tar was benzene insoluble to begin with. At this point it would seem that a product recycle as a solvent (when tar was the solvent) would be undesirable in a commercial plant because this would result in low conversions. Perhaps the best solvent would be

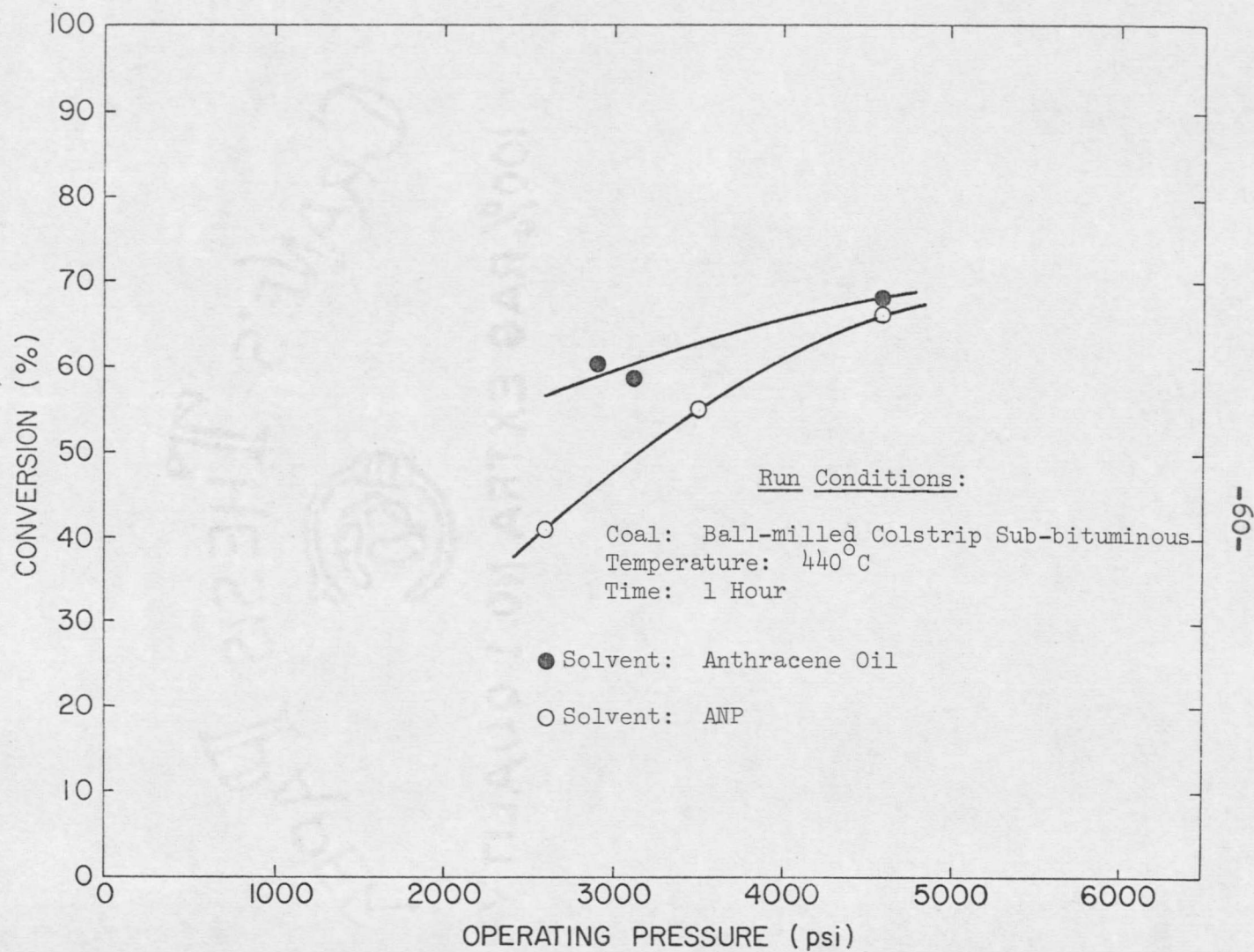


Figure 17: Interaction of Operating Pressure and Solvent on Conversion.

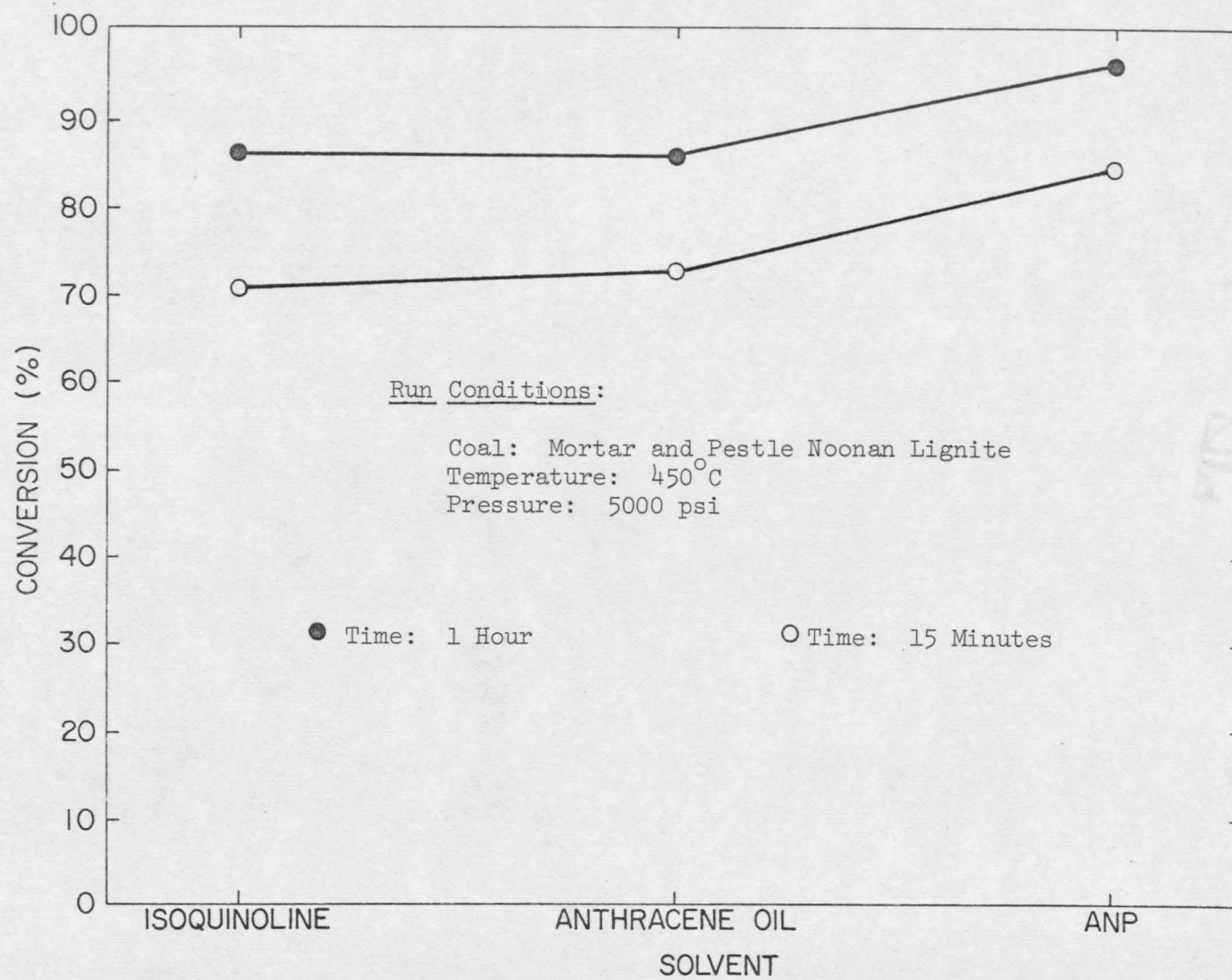


Figure 18. Conversion Versus Type of Solvent with Noonan Lignite.

anthracene oil since it does give good conversions and is inexpensive when compared to the cost of isoquinoline and ANP.

6. Effect of CO cycles on conversion:

One method that was explored in an attempt to increase conversion was to add fresh CO to the reaction from time to time. This was done by making a normal run and then removing the gas from the reactor after it had cooled. Then a fresh supply of CO was added to the autoclave and a second run was made, or two cycles of CO were added.

At first it appeared that we were obtaining quite satisfactory results through the use of this method (Figure 19), and several runs were made. But the total residence time of the coal in the autoclave increased and this had to be taken into account.

A run using one cycle and a three hour residence time was made and was then compared to a run made with three cycles, each one hour long. The three cycles run produced conversions that were about ten percent higher than the conversion seen in the one cycle run (Figure 20). Then a three cycle run with the residence time of each cycle lasting ten minutes was made and conversion was about

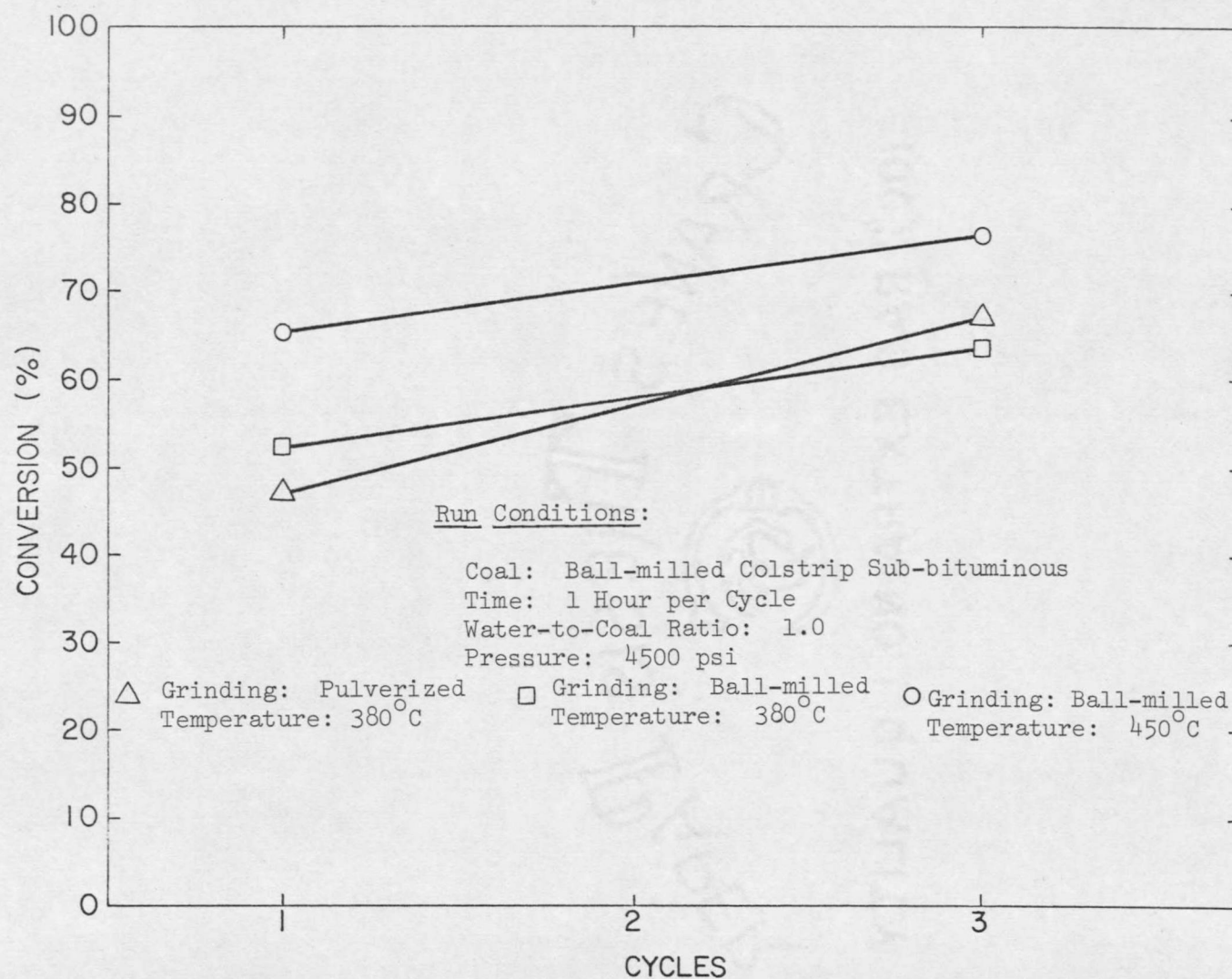


Figure 19. Conversion Versus Numbers of Cycles of CO Addition to the Autoclave.

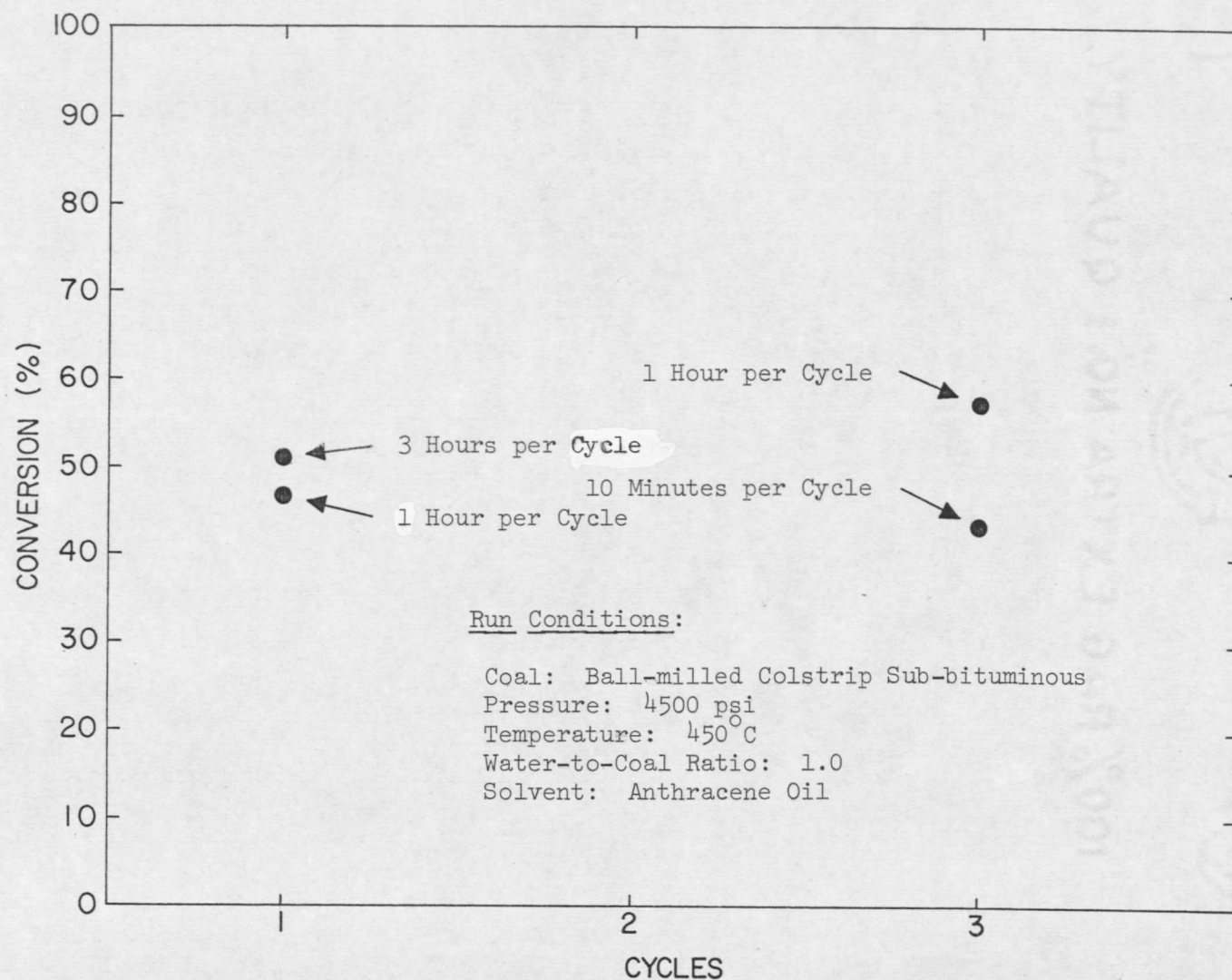


Figure 20. Comparison of Runs Made to Show Effect of Number of Cycles and Total Residence Time on Conversion.

ten percent lower than the conversion obtained from a one cycle, one hour run. Therefore, it does appear that this sort of cycle method does have some advantage, but it is hard to be definite about the statement. The reason is that during the heating of the autoclave to temperature, reaction is taking place. Therefore, a ten minute run may have significant reaction taking place for an additional 30 minutes while the autoclave is heating and cooling. The reason for the slight increase in conversion would probably be due to the fact that the water-gas shift reaction would be taking place quite rapidly at the start of a new cycle, thereby making more nascent hydrogen available to the coal.

7. Effect of grinding methods on conversion:

At first pulverized coal was used but it was thought that aging (oxidation and loss of moisture) of the coal may have had an adverse effect on conversion. Therefore, coal ground in a ball mill was used and compared with the reaction of pulverized coal (Figure 21). An improvement was noted.

The ball-milled coal, when compared to sub-bituminous coal's black color, still looked brown after it came out

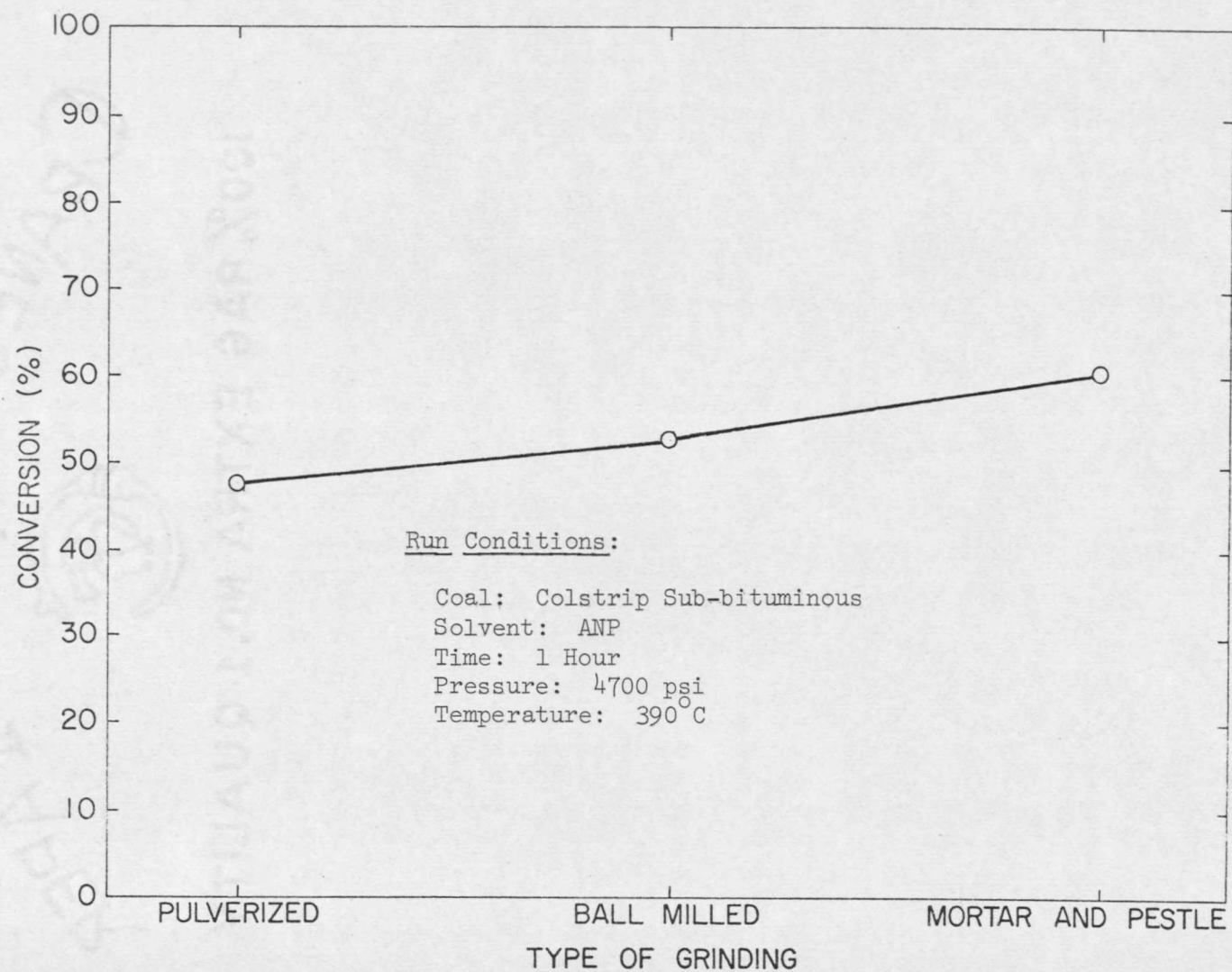


Figure 21. Conversion Versus Type of Grinding Using Colstrip Sub-bituminous.

of the ball mill, so the coal was then ground using a mortar and pestle, hoping to prevent aging.. Again an improvement was noted which was probably due to shorter contact with air.

In a commercial process of coal liquefaction using the water-gas shift reaction it would be desirable not to dry the coal before it is added to the reactor in order to prevent aging. Also, grinding should be kept to a minimum.

8. Effect of coal type on conversion:

The results obtained when different types of coal were examined under the same condition is shown in the same manner as used in Figure 21 (see Figure 22). The results show that lignite is more reactive than sub-bituminous, but even the three lignites give quite different results. Noonan lignite is more reactive than Stanton lignite which is more reactive than Savage lignite. The dashed lines indicate what conversions based on experimental results would be expected by using other grinding methods.

The reasons for these differences will be discussed after the results of the gas analyses are described.

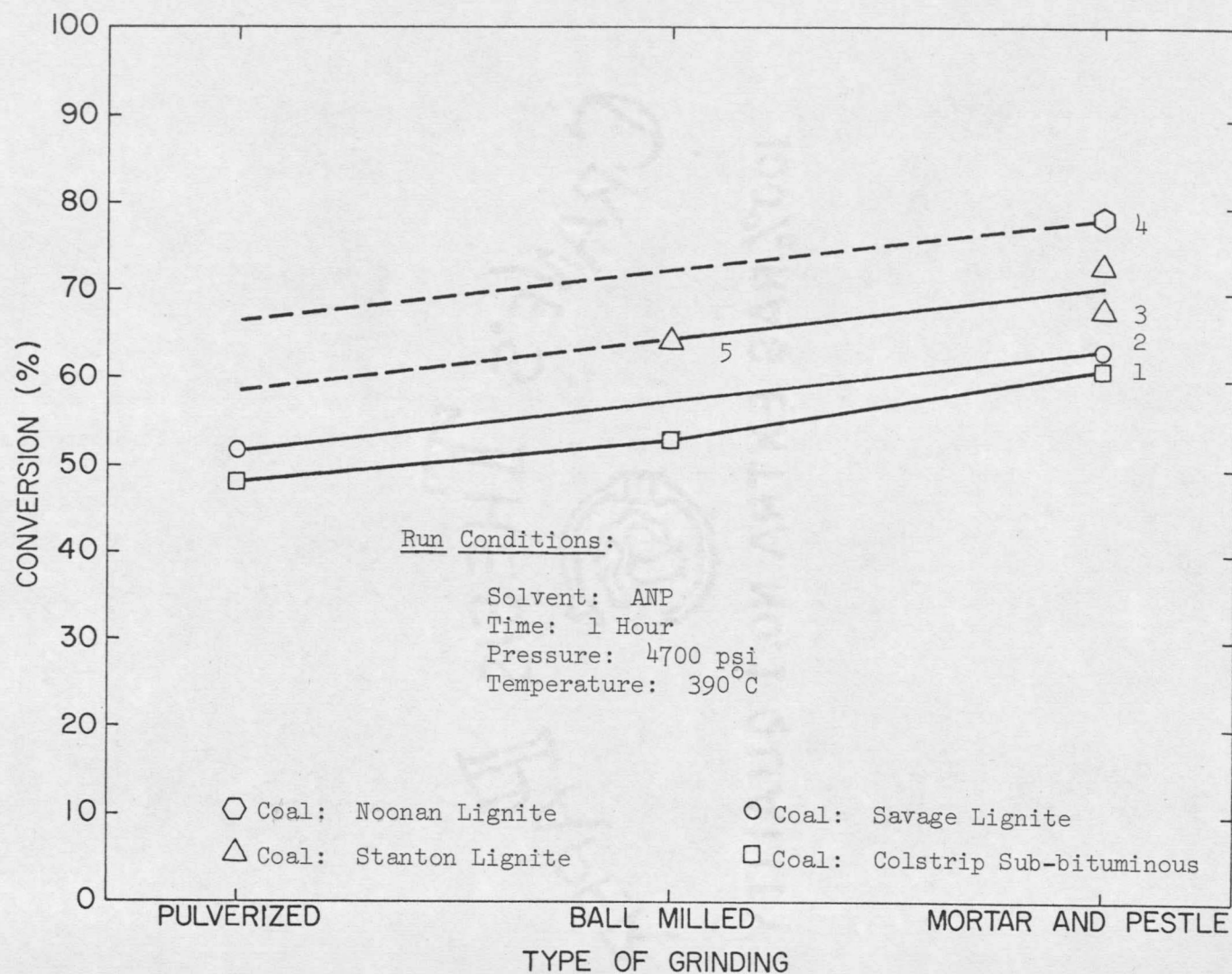


Figure 22. Effect of Type of Coal and Type of Grinding on Conversion.

9. Effect of CO-to-coal ratio on conversion:

Even though the autoclave had a volume of 500 ml, due to the physical structure of the autoclave and the foaming of the liquid products, only 50 grams of coal could be reacted. If less than 30 grams was used, it was felt that this would represent an insufficient amount of material on which an accurate analysis of conversion could be made.

Increasing the coal charge from 30 grams to 50 grams made very little difference in conversion results. Under the same conditions, the conversion for 30 grams was 64.5% and 65.4% for 50 grams.

The CO-to-coal ratio in the autoclave was calculated to be 1.74 grams for CO per gram of coal when 30 grams of coal were used, and 1.20 grams of CO per gram of coal when 50 grams of coal were used. The minimum theoretical ratio to obtain 90% conversion has been calculated to be 0.11 grams of CO per gram of coal. Therefore, even with 50 grams of coal, it appears that there is more than enough CO available in the autoclave to obtain maximum conversion under given conditions. It is desirable to have the CO-to-coal ratio as small as possible since it would reduce the size of the reactor that would be needed.

10. Effect of mixing on conversion:

The rocking mechanism on the autoclave was quite slow, but we still wanted to see what the effect would be if no rocking action was used (static condition).

With all conditions being the same, a 39.8% conversion was obtained with the reactor in a static condition and a 60.5% conversion was obtained with the rocker on. During the preliminary runs, a run was made with hydrogen on Savage lignite under the same conditions as were used in another research project where a stirred autoclave was used. In the rocking bomb experiment, 35.5% conversion was obtained while in the stirred autoclave about 85% conversion was obtained (40). Although no catalyst was used in either of the experiments, the stirred autoclave was used for catalytic studies from time to time and may have had catalytic contamination from previous experiments. Nonetheless, these facts do point out that the conversion results obtained from the rocking autoclave should be considered as very conservative. The reason for this is that the reaction involved a gas-slurry type of reaction, and the greater the mixing, the better the contact between the gas and slurry. This is especially true when a short lived

intermediate such as nascent hydrogen is involved.

11. Overall improvements in conversion:

When the first runs were made, pulverized Savage lignite was used with very little success. By applying what we had learned from the above results, conversions increased to the point where it could at least be considered possible to use the reaction in a commercial process. By increasing the temperature, using coal ground in a mortar and pestle, and by switching to Noonan lignite, conversions in the 80 to 90 percent range could be made in relatively short reaction times (Figure 23).

12. General run characteristics:

The most complete investigation on any of the coals in this study was made on Noonan lignite. The effects of solvent, time, and temperature are all shown in Figure 24. It appears that at about one hour reaction time the conversion is essentially completed since the conversion after one hour is about the same as it is after two hours. Also, the amount of conversion that takes place before reaction temperature has been reached is shown for 450°C and 380°C. From the above results the trends of conversion for Noonan lignite were fairly well determined. It was assumed that

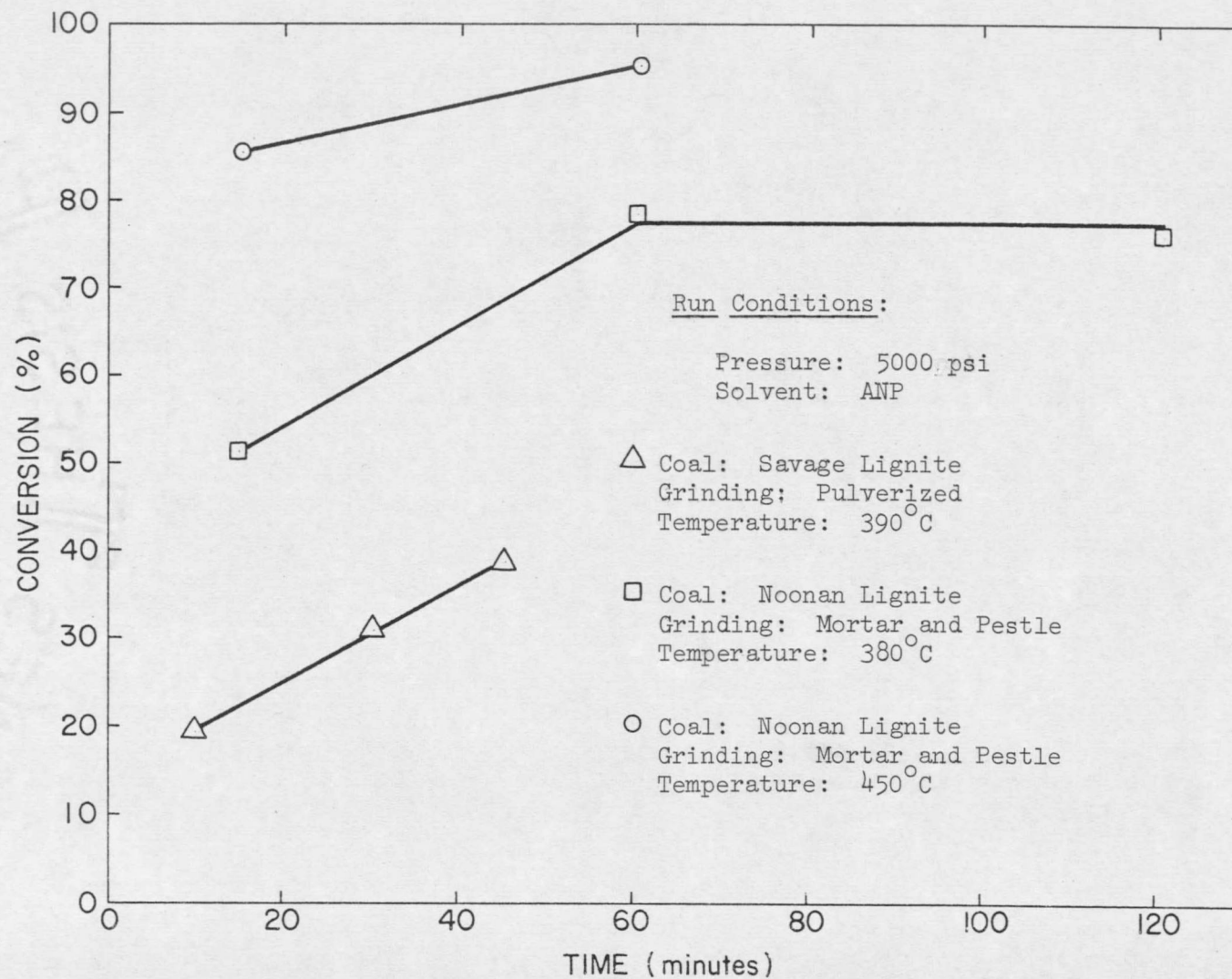


Figure 23. Overall Improvement of Conversion of Lignites from the Start of the Study to the End of the Study.

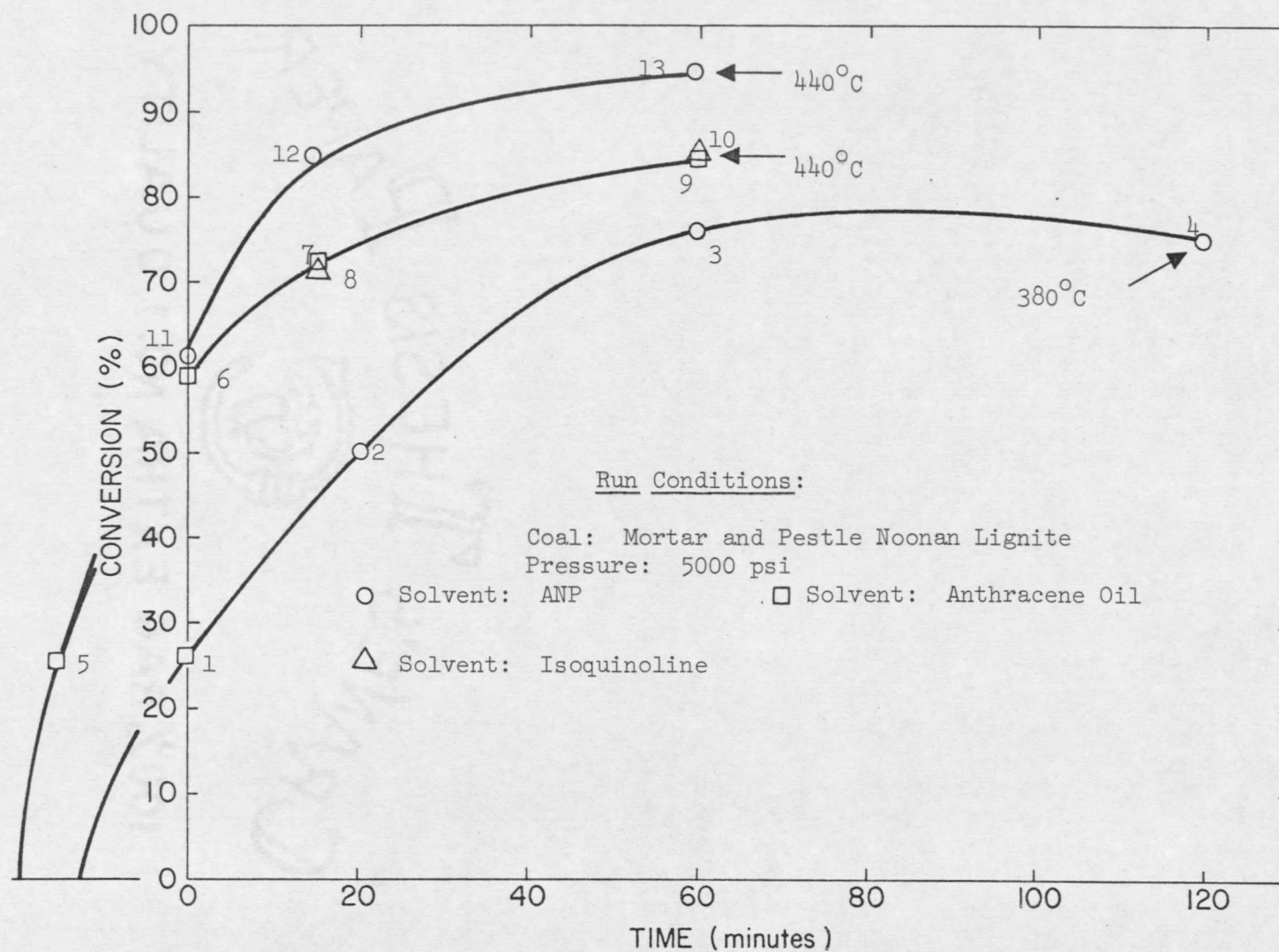


Figure 24. Effects of Time, Solvent, and Temperature on Conversion of Noonan Lignite.

Savage lignite and Colstrip sub-bituminous coal would behave in a similar manner. However, additional information about the conversion of Savage lignite and Colstrip sub-bituminous coal was needed. The runs made on these two coals where conversions were expected to be below 60% or which required reaction times of greater than one hour were considered to be undesirable for use in a commercial plant design study. Figure 25 does show that conversion is less for Savage lignite than for Noonan lignite when the same conditions are used. Colstrip sub-bituminous does not convert to as much benzene soluble material as the lignite coals do. This is especially true at higher temperatures (Figure 26). The other trend, of course, is that anthracene oil is a better solvent than ANP for sub-bituminous coal and vice versa for lignites.

B. Results and Discussion of Gas Analyses.

The gas analyses proved to be very valuable in determining what was happening inside the autoclave. Unfortunately, gas analyses were not being made during the first 35 runs since the gas analysis system was being designed and developed at that time.

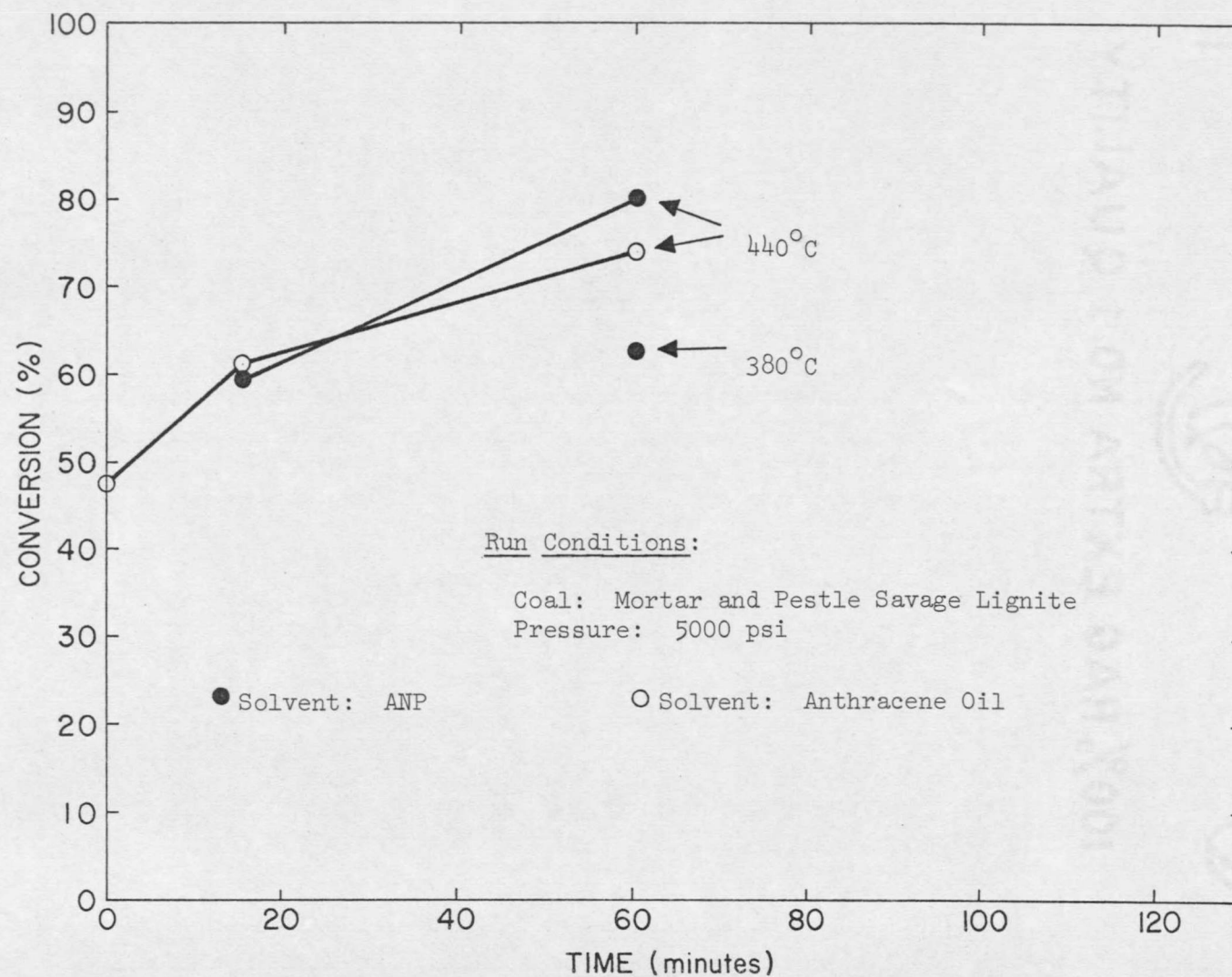


Figure 25. Effects of Time, Solvent, and Temperature on Conversion of Savage Lignite.

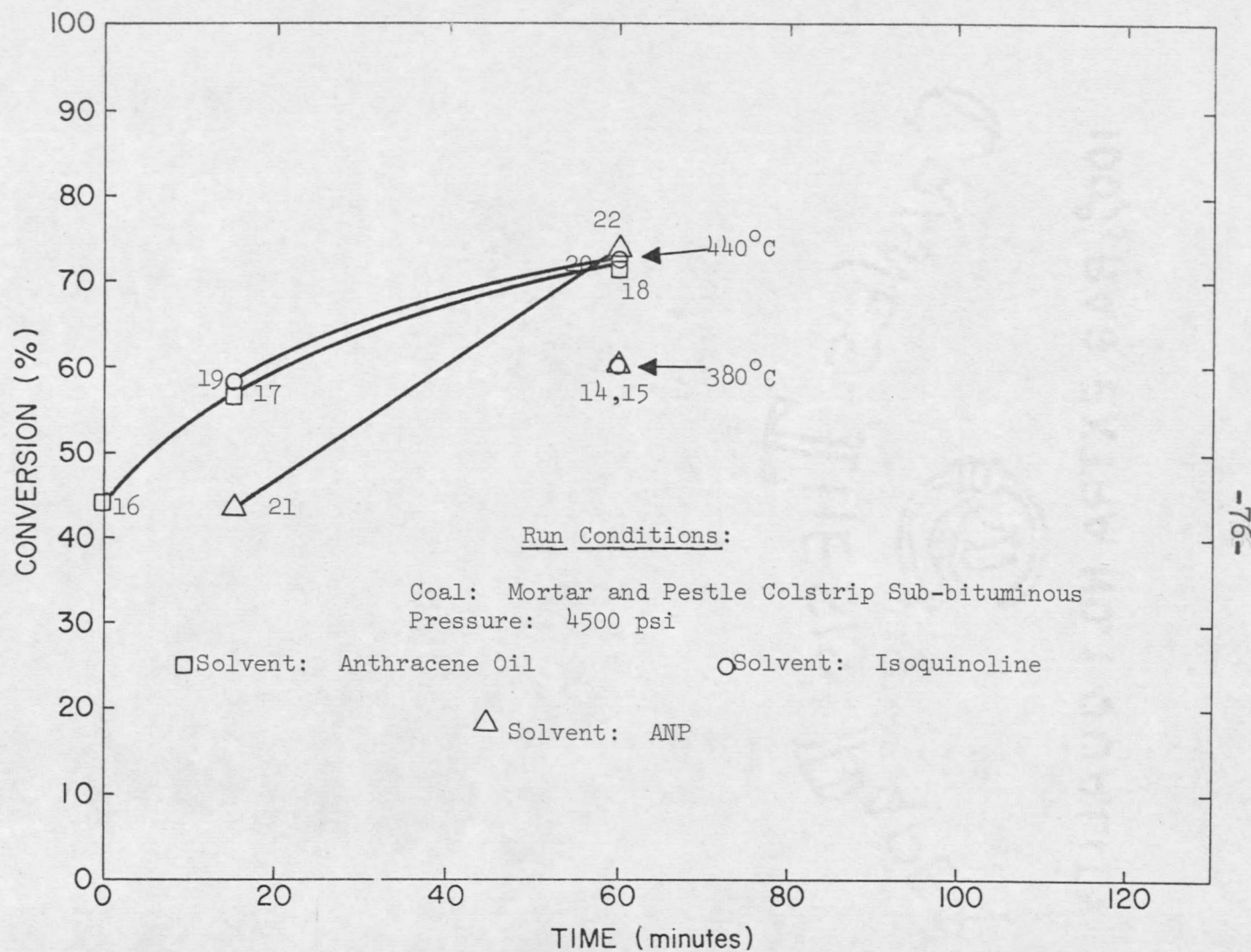


Figure 26. Effect of Time, Solvent, and Temperature on Conversion of Colstrip Sub-bituminous.

1. Effect of Solvents, temperature, and time on gas analyses:

Gas analyses were made on all of the runs which used Noonan lignite, and the same trends in the gas analyses were noted for the other coals. Therefore, only the results of the Noonan lignite and the Colstrip sub-bituminous runs will be presented in detail when considering the variables of solvent, temperature, and time.

The runs in Figure 24 are numbered, and the concentrations of CO, CO₂, and H₂ for the runs are given in Table III. In most cases the CO concentration decreases and CO₂ and H₂ concentrations increase with increasing conversion. Thus the shift reaction had gone further to completion when conversions were higher, thereby producing more available hydrogen. Also, some CO₂ was produced from the coal itself and under these conditions it would be nearly impossible to say how much CO₂ comes from the coal and how much comes from the water-gas shift reaction. There are methods for determining the amount of CO₂ in the mineral matter as carbonates, but some CO₂ probably comes from the organic oxygenated material in the coal as well.

Figure 16 is also numbered and the gas analyses for these runs are given in Table III. The same general trends

TABLE III. Gas Analyses on an Air-free Basis of Noonan Lignite and Colstrip Sub-bituminous.

<u>Run</u>	<u>CO</u>	<u>CO₂</u>	<u>H₂</u>
Noonan Lignite:			
1	86.8%	5.3%	7.8%
2	85.5	5.4	9.1
3	----	----	----
4	58.6	23.4	18.0
5	52.3	25.65	22.2
6	85.5	5.4	9.1
7	70.8	13.65	15.65
8	56.6	22.4	19.5
9	61.65	25.6	11.9
10	39.3	31.8	29.1
11	60.8	28.1	9.4
12	71.4	15.7	12.5
13	50.1	28.65	21.0
14	35.2	38.1	25.2
Colstrip Sub-bituminous			
15	78.4	14.65	7.0
16	----	----	----
17	88.8	7.4	3.8
18	68.4	15.9	15.3
19	70.1	19.0	9.0
20	84.1	12.3	2.9
21	69.8	21.4	7.7
22	77.4	11.3	11.1
23	71.1	18.5	9.6

are noted for sub-bituminous coals as are noted when using Noonan lignite..

The water-gas shift reaction was nearer equilibrium with the rocker on. When the rocker was off, the CO concentration was 83.8%, while with the rocker on, the CO concentration was 70.8%, with corresponding changes in CO₂ and H₂ concentrations..

2. Effect of type of coal on gas analyses:

The conversion of coal to a benzene soluble material and the completion to equilibrium of the water-gas shift reaction were quite different for each lignite used. The runs in which gas analyses were made are numbered on Figure 22. Even though the coals were of different grades, the gas analyses for sub-bituminous and Savage lignite were about the same (Table IV). However, the water-gas shift reaction was more productive with Stanton lignite than with Savage lignite and the reaction was even more complete when Noonan lignite was used..

It is noted that the ash in the coal acts as catalysts for the water-gas shift reaction. Iron has more of a catalytic effect than any other element in the ash. In fact it was stated that Fe₂O₃ and Na₂CO₃ have been shown

TABLE IV. Gas Analyses of Different Coals at the Same Conditions.

<u>Run</u>	<u>CO</u>	<u>CO₂</u>	<u>H₂</u>
1	78.4%	14.6%	7.0%
2	79.4	13.1	7.4
3	63.0	13.4	12.8
4	58.6	23.4	18.0
5	96.7	17.5	7.8

to have a catalytic effect, but silica, alumina, or fire-clay did not appear to have this effect (41). However, the iron oxide concentration in all of the coals used in this study is about the same (Table I). The major difference is the Na_2O concentration, and an increase in the sodium concentration in the ash of the coal corresponds to an increase in conversion. The sodium in the ash has been shown to be evenly dispersed throughout the coal in the form of a salt of a humic acid (42). With the aid of sodium and iron, the shift reaction would probably take place on the coal thereby making nascent hydrogen readily available at the reaction site.

3. Analyses of hydrocarbon gases:

In all of the coal runs, hydrocarbon gases (C_1 through C_4) were produced in various amounts depending upon conditions of the runs. However, hydrocarbon gas production is such that the concentration of these gases is less than that of the other three main constituents (CO , CO_2 , and H_2) and it was very hard to obtain an accurate determination of concentrations. Therefore there was considerable scatter in the results, but general trends could still be seen.

In the first few runs where gas analyses were made,

it was obvious that the C_3 and C_4 hydrocarbon gases were produced only in trace amounts, and were not recorded in later runs. Only concentrations of methane and ethane were determined.

The increase in conversion of coal to methane and ethane increased significantly with increased time and temperature. The amount of methane and ethane in a long time and high temperature run would be typically 1.3% and 0.3% respectively. A typical analysis of these two variables is shown in Table VI.

If one percent of the reaction gases is methane, it was calculated that this corresponds to about 1.5% of the coal reacted to form methane. Thus, for a long time, high temperature run it appears that no more than four percent of the coal goes to hydrocarbon gases and no more than one percent of the coal converts to hydrocarbon gases in a short time, high temperature run.

4. Gas analyses for cycle runs:

Shown in Table VI are the gas analyses for a three cycle run. During the first cycle, the greatest conversion takes place, with perhaps up to 50% of the organic portion of the coal going to a benzene soluble material, then

TABLE W. Concentration of Methane and Ethane From a Typical Run Series.

Run Conditions:

Coal: Noonan lignite

Pressure: 5000 psi

Solvent: ANP

Grinding Method: Mortar and Pestle

	<u>Low Temperature</u>		<u>High Temperature</u>	
Short Time (15 Minutes)	methane	trace	methane	0.33%
	ethane	trace	ethane	0.09%
Long Time (1 Hour)	methane	0.5%	methane	1.0%
	ethane	trace	ethane	0.4%

TABLE VII. Results of Gas Analyses for Cycle Runs.

Run Conditions:

Coal: Colstrip Sub-bituminous
Temperature: 4700 psi
Pressure: 450°C
Solvent: ANP
Grinding Method: Ball-milled

<u>Gas</u>	<u>Cycle A</u>	<u>Cycle B</u>	<u>Cycle C</u>
CO	73.9%	82.8%	86.5%
CO ₂	15.8	9.8	7.3
H ₂	10.0	8.3	5.8
CH ₄	0.20	0.11	0.07

conversion will probably increase five percent in each of the other two cycles (Figure 20). The water-gas shift reaction was not as complete in cycle B as it was in A, nor was it as complete in C as it was in B. However, even though increase in conversion of the coal was rather small in the last two injections, the water-gas shift reaction was still taking place at a respectable rate. This would indicate that the catalysts in the coal are still somewhat active to initiate the shift reaction in the last two cycles.

5. Analyses of gas runs without coal:

Since it was known that the sodium and iron in the ash may have an effect on conversion, some runs were made just with CO and water along with sodium carbonate and iron oxide.

The results of these three runs are indicated in Table VII. In run GAS-2, five grams of iron oxide were added to the autoclave, and in GAS-3, five grams of sodium carbonate were added.

If no catalyst were used the shift reaction did not take place to any great degree. If, however, iron oxide is added, some reaction does occur. Sodium carbonate is found to be an even more effective catalyst. This supports

TABLE VII. Results of Gas Runs without Coal.

Run Conditions:

Time: 1 Hour
Temperature: 385°C
Pressure: 5000 psi

<u>Run</u>	<u>CO</u>	<u>CO₂</u>	<u>H₂</u>	<u>Catalyst</u>
GAS-1	93.2%	2.7%	3.2%	none
GAS-2	78.5	5.2	15.4	Fe ₂ O ₃
GAS-3	45.8	22.7	30.65	Na ₂ CO ₃

the fact that the sodium and iron in the coal does catalyze the water-gas shift reaction.

It is noted that in all of these runs the hydrogen concentration is higher than the CO_2 concentration, when they should actually be the same. In the early gas runs, water bottles were used to store the reaction gas sample and it was believed that the CO_2 was absorbed in the water. This was not the case in later runs when the 20 gallon drum was used for gas storage.

C. Product and Residue Analyses.

The hydrogenated product was analyzed by Huffman Laboratories since they could make the analyses through the use of micro techniques. Our laboratory was not equipped to make this kind of analysis. The analyses were quite expensive; as a result only two complete analyses were made, one from the hydrogenated product produced from Savage lignite and one from Colstrip sub-bituminous' hydrogenated product.

The ultimate analyses and the molecular weight determinations for the two coals are shown in Table VII. The molecular hydrogen-to-carbon ratio for the product ranged from 1.10 to 1.17 and the ash content was very low (less

TABLE VIII. Proximate and Ultimate Analyses, and Molecular Weight Determinations of Hydrogenated Product and Char.

<u>Analysis</u>	<u>Residue</u>	<u>Savage Lignite Product</u>	<u>Colstrip Product</u>
Proximate			
Water	1.2%		
Volatile	19.5		
Fixed Carbon	49.7		
Ash	29.6		
Ultimate			
Ash	29.7	.10	.02
Hydrogen	3.3	8.09	7.71
Carbon	56.6	82.88	84.10
Sulfur	0.3	5.0	.24
Nitrogen	1.0	0.99	1.86
Oxygen	9.1	----	6.07
Molecular Weight		414	365

than 0.1%). Also the molecular weight is quite high and it appears from these results that the hydrogenated product has the characteristics of a tar. In fact it seems that if we assume the structure shown in Figure 3 to be similar to that of the coals studied, it appears that only the bonds linking the ring structures are broken. Thus, the product would probably consist of the large multi-ringed structures shown in Figure 3.

The only unexpected value of these analyses is the sulfur analysis of the tar from the Savage lignite which is 5.0% compared to the expected value of 0.2%. The reason for this discrepancy can be explained by the fact that coal contains both pyritic sulfur and organic sulfur (43). The large percentage of sulfur in this sample was probably due to the additional pyritic sulfur (which sometimes is seen visually) in the particular coal sample used.

The proximate and ultimate analyses of the char products (or residue) is given in Table VIII. When compared to coal, the hydrogen content had decreased while the ash content increased considerably. It is also worth noting that the char contains some volatile matter which could be driven off by heating in the absence of air to obtain more tar and oil. These ultimate analyses are similar to those

obtained by the United States Bureau of Mines when they used Noonan lignite (35).

D. Runs with Sodium Carbonate as a Catalyst.

After learning of the desirable effects of Na_2CO_3 on the shift reaction, this chemical was added to the coal to serve as a catalytic agent. Sodium carbonate was added to Colstrip sub-bituminous and Savage lignite coals (both low in sodium) so that the total sodium content in these two coals would be the same as the high sodium content found in Noonan lignite.

The conversion for both coals increased; this was noted especially when the Colstrip sub-bituminous coal was used (Figures 27 and 28). The increase was greater for the sub-bituminous coal because anthracene oil is found to be the best solvent for this coal. Savage lignite on the other hand did not increase in conversion as much because anthracene oil is not as effective a solvent as ANP is for this particular coal. If ANP had been used as a solvent for the Savage lignite with Na_2CO_3 , the conversion probably would have been much better.

The gas analyses show an increased consumption of CO ,

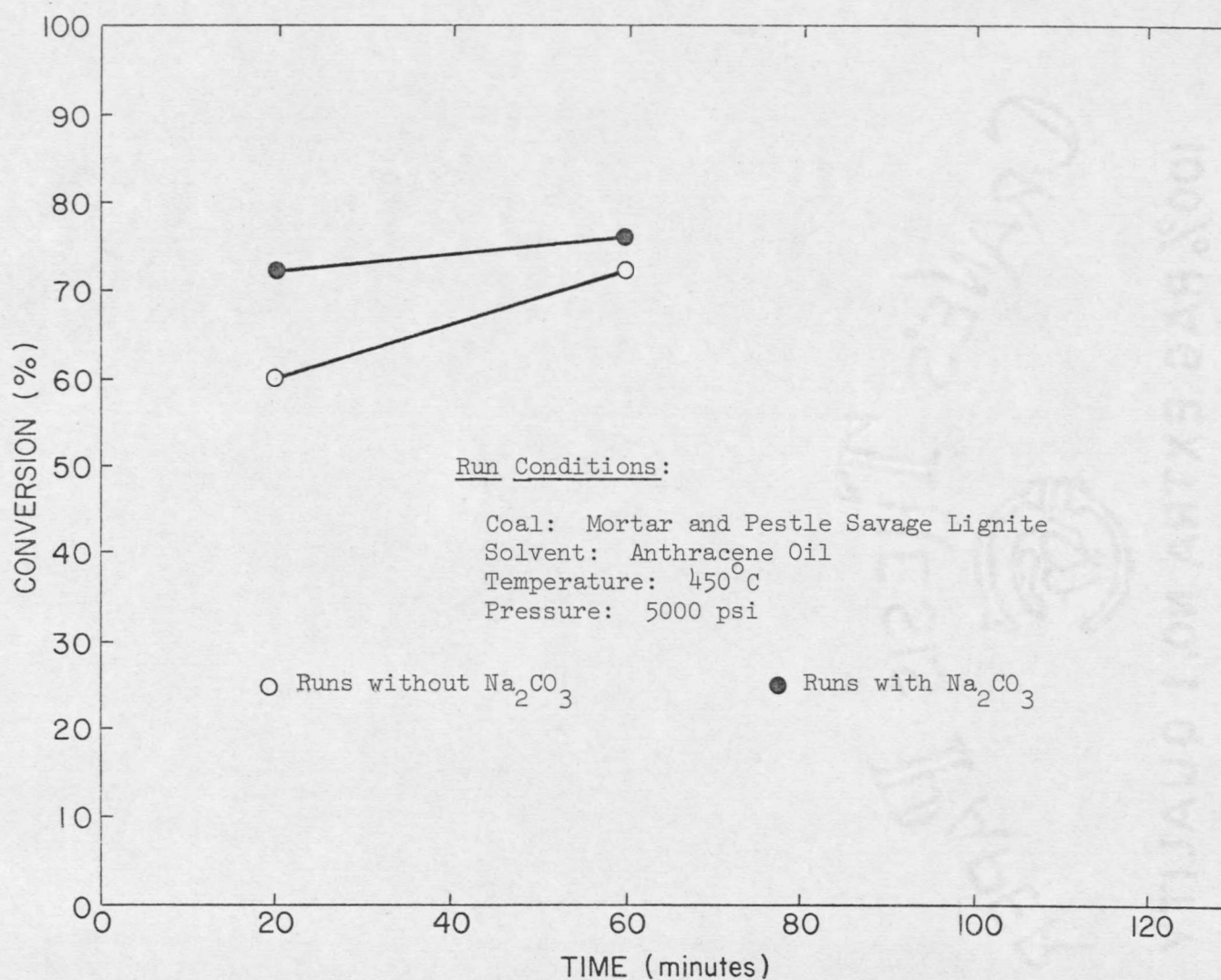


Figure 27. Comparison of Conversions with Sodium Carbonate and without Sodium Carbonate using Savage Lignite.

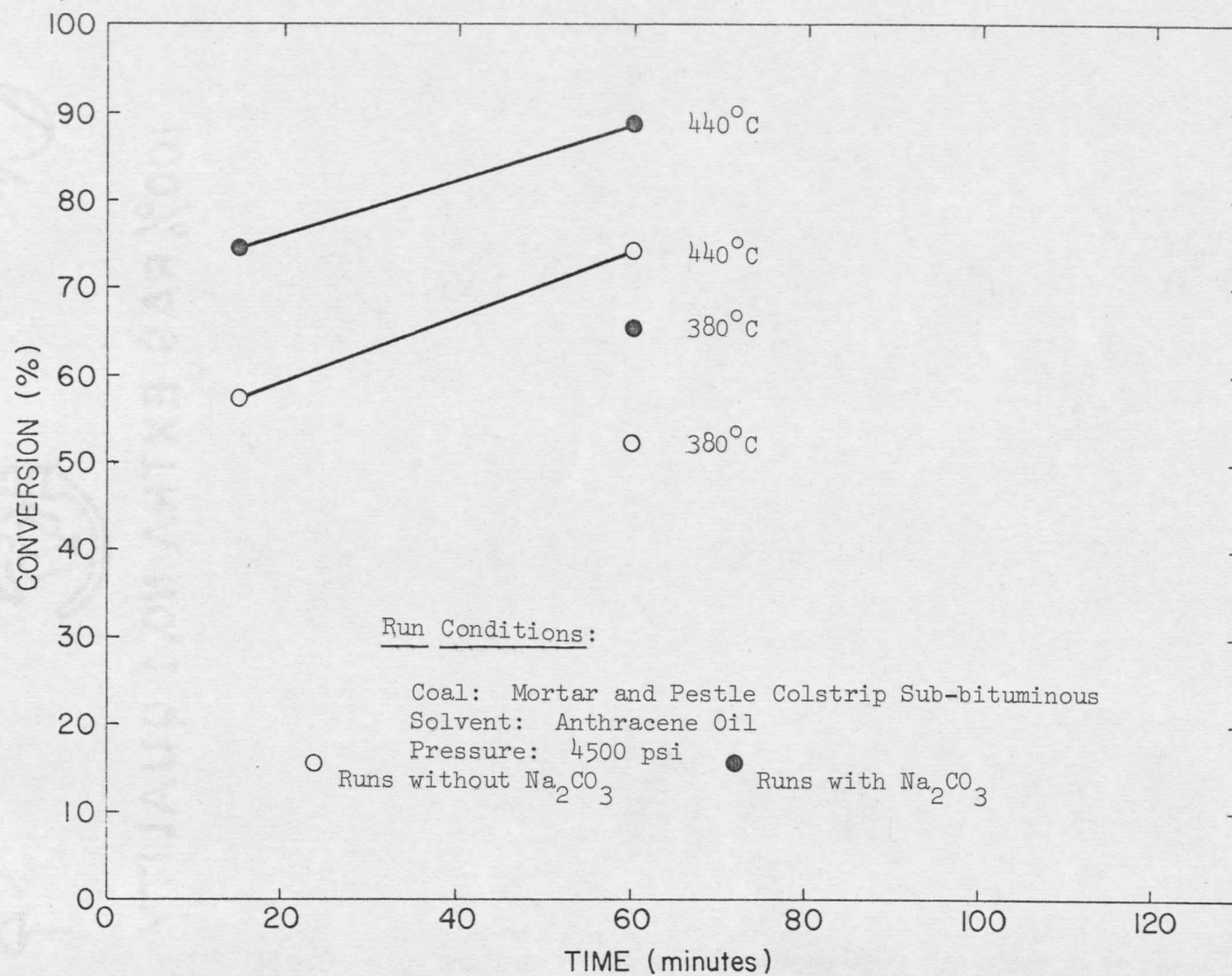


Figure 28. Comparison of Conversions with Sodium Carbonate and without Sodium Carbonate using Colstrip Sub-bituminous.

which was expected (Table IX).

E. Runs with Materials Other Than Coal.

Several runs were made with cellulose, Bunker C fuel oil, and asphalt to see if any information about the conversion of coal to tar via the shift reaction could be obtained. Run A, which used Colstrip sub-bituminous, shown in Table X, is placed there for comparison with results obtained when materials other than coal were used in the water-gas shift reaction.

The cellulose used in run B was used because it may have a structure similar to coal, and it contains a small amount of ash and a large amount of oxygen. The ash content of the cellulose was 0.13% and about 7.6% of that ash is Na_2O . Asphalt and Bunker C, which were used in runs C and D respectively, were low in both oxygen and ash. Run E was the same as D except that Na_2CO_3 was added to act as an artificial ash which would be high in sodium.

The gas analysis for each of these runs is shown in the same table. The results of these runs tend to show that there is no direct relationship between oxygen content and the degree to which the water-gas shift reaction will take place. If this were the case, the concentration of

TABLE IX. Gas Analyses of Coal Runs With and Without Na_2CO_3 .

Run Conditions:

Solvent: Anthracene Oil

Pressure: 4800 psi.

Temperature: 450°C

Coal: Sub-bituminous Time: 15 Minutes			Coal: Sub-bituminous Time: 1 Hour		
Without Na_2CO_3	Gas	With Na_2CO_3	Without Na_2CO_3	Gas	With Na_2CO_3
68.4%	CO	55.6%	70.1%	CO	38.6%
15.9	CO_2	26.2	19.0	CO_2	31.9
15.3	H_2	17.4	9.0	H_2	28.6
0.4	CH_4	0.8	1.3	CH_4	0.7
0.1	C_2H_6	0.1	0.6	C_2H_6	0.2

Coal: Savage Lignite Time: 15 Minutes			Coal: Savage Lignite Time: 1 Hour		
Without Na_2CO_3	Gas	With Na_2CO_3	Without Na_2CO_3	Gas	With Na_2CO_3
78.7%	CO	67.9%	79.5%	CO	58.9%
12.5	CO_2	17.4	9.4	CO_2	22.5
8.8	H_2	14.9	10.8	H_2	17.5
0.1	CH_4	0.4	0.3	CH_4	0.9
----	C_2H_6	0.1	----	C_2H_6	0.2

TABLE X. Properties of Materials Reacted with CO and H₂O, and the Resulting Run Gas Analyses.

Run Conditions:

Time: 1 Hour
 Pressure: 1500 psi Initial
 Temperature: 450°C
 Water: 15 Grams

<u>Run</u>	<u>Properties of Materials</u>				<u>Gas Analyses</u>			
	<u>Material</u>	<u>% O in Material</u>	<u>% Ash in Material</u>	<u>% Na₂O in Material</u>	<u>% CO</u>	<u>% CO₂</u>	<u>% H₂</u>	<u>% CH₄</u>
A	Sub-bituminous	13.7	7.6	.014	82.8	10.3	5.3	0.4
B	Cellulose	49.4	.13	.009	87.4	5.7	7.0	trace
C	Asphalt	0.6	.105	----	94.7	1.9	1.9	1.1
D	Bunker C	0.4	.04	----	97.6	0.8	0.8	0.8
E	Bunker C with Na ₂ CO ₃	0.4	2.4	1.46	64.7	19.5	14.8	0.8

CO in the gas analysis of run B would be greater than the CO concentration found in run A.

The other factor that was considered to have an effect on the degree of conversion of the shift reaction, was the quality and quantity of the ash in the material being reacted. It was not known what the ash composition for the Bunker C was, but the ash analyses of oil is roughly the same as that of coal (44). Bunker C has less ash in it than any of the materials reacted, and the shift reaction did not produce good yields of hydrogen. Asphalt contained more ash and the shift reaction yield of hydrogen was better than that seen when Bunker C was used.

The shift reaction produced better yields using cellulose rather than asphalt, but Colstrip sub-bituminous produced only slightly better yields even though the coal has considerably more ash. However, if the amount of sodium in the ash is considered, Colstrip coal had only slightly greater sodium content than cellulose has. It appears that the amount of sodium in the material being reacted via the water-gas shift reaction is the contributory factor in determining how well the CO and H₂O react to form H₂ and CO₂.

To serve as a check, one gram of Na₂CO₃ was added to 40 grams of Bunker C to act as a synthetic high sodium ash.

The results again show a significant yield of CO_2 and H_2 from CO and H_2O thus confirming the above hypothesis that ash quality and quantity contribute to a productive water-gas shift reaction.

The results found when samples of Bunker C and asphalt were reacted with CO and H_2O , and in some cases with Na_2CO_3 , are shown in Table XI. The original Bunker C had a hydrogen-to-carbon ratio of 1.53 before reaction. After the reaction with CO and H_2O (run D), the Bunker C hydrogen-to-carbon ratio decreased to 1.38. The reason for this is that the original hydrogen in the Bunker C went to form methane, and that there was very little hydrogen produced by the shift reaction to make up for the hydrogen losses in the Bunker C incurred by methane production.

When Bunker C was reacted with CO , H_2O , and Na_2CO_3 (run E), the hydrogen-to-carbon ratio was 1.47. It is noted that the methane production was the same as that seen in run D (Table X). This would indicate that the production of methane was not retarded. Rather, the hydrogen produced by the shift reaction was added to the Bunker C, thereby making up for some of Bunker C's hydrogen losses caused by methane production. The same general trends were noted when asphalt was used.

TABLE XI. Elemental Analyses of Bunker C and Asphalt.

A. Elemental analysis of reacted asphalt and Bunker C products.

	<u>Asphalt</u> <u>Without Na_2CO_3</u>	<u>Asphalt</u> <u>With Na_2CO_3</u>	<u>Bunker C</u> <u>Without Na_2CO_3</u>	<u>Bunker C</u> <u>With Na_2CO_3</u>
C	86.2	84.5	86.7	86.8
H	9.8	9.9	9.9	10.6
N	1.0	0.8	0.5	0.5
S	2.9	2.8	2.1	2.0

B. Hydrogen-to-carbon ratios of Bunker C and asphalt before and after reaction with CO and H_2O .

	<u>Bunker C</u>	<u>Asphalt</u>
Before treatment	$\text{C}_1\text{H}_{1.53}$	$\text{C}_1\text{H}_{1.45}$
Treatment with CO + H_2O at 450°C , 1 hour, 5000 psi	$\text{C}_1\text{H}_{1.38}$	$\text{C}_1\text{H}_{1.37}$
Treatment with CO + H_2O + Na_2CO_3 at 450°C , 1 hour, 5000 psi	$\text{C}_1\text{H}_{1.47}$	$\text{C}_1\text{H}_{1.41}$

It is noted that there was essentially no sulfur or nitrogen removal from these products. This was noted in the coal runs as well.

F. General Mechanism

Weller, Clark, and Pelipetz proposed a mechanism of coal hydrogenation (45) which this author believes is a very good one. The weaker bonds between the aromatic ring cluster are broken by a thermal depolymerization reaction, forming reactive fragments. These fragments may either recombine to form larger, less reactive fragments, or they can be stabilized and go into solution in the solvent.

With this information, a general mechanism can be proposed which would explain the observations we have made on the conversion and gas analyses. After the thermal depolymerization reaction, the fragments must be stabilized with hydrogen if they are to be soluble in the solvent. Since the sodium, and probably the iron, are bound evenly throughout the coal, they are very near to or even in the fragments themselves. With the aid of these catalysts in the coal, the water-gas shift reaction takes place and nascent hydrogen is readily available to stabilize the fragments.

The aromatic ring cluster does not appear to be broken because of the high molecular weight of the product, at least to any great extent. Again, the characteristics of the solvent determines if the fragments will become soluble in the solvent. It is very difficult to say exactly what is happening, since the structure of these low grade coals is not precisely known.

These results and general mechanism do not in any way discount the findings of Appell and Wender, but simply add to what they found. This explains how the activated hydrogen becomes available, and why it works well on some coals and not on others. The other points that they present, the introduction of alkyl groups, and the ability of CO to cleave bonds or inhibit condensation reactions leading to benzene-insoluble products, though unlikely, could be contributing factors for this reaction's effectiveness. For example, the aging of the coal may have an effect on how many alkyl groups are in the coal, thereby having an effect on conversion.

VI. PLANT DESIGN AND ECONOMICS

The primary reason for doing the experimental work was to obtain information leading to the design and economic evaluation of a commercial plant. From the information obtained from this research and from reports which evaluate existing coal hydrogenation processes, it was felt that a good estimate of the costs of producing tar via the water-gas shift reaction could be made.

There are many uses for a tar product produced from coal. For example, the tar is considered a deashed coal and can be burned in steam generating plants thus resulting in the elimination of a need for an ash collecting system. The tar can also be used to produce electrode carbon; can be used as a fuel for fuel cells, or can be further hydrogenated to produce a synthetic crude oil (46). As has been mentioned in the introduction, the lower the hydrogen content, and particularly the lower the ash content in the fuel, the more desirable it is for use as a MHD fuel. The analysis of the tar product shows that it is low in hydrogen and does have a low ash content; therefore, it should be an ideal fuel for MHD.

Two liquefaction processes which use existing knowledge

of coal hydrogenation processes and information obtained from this experimental work are proposed as a result of this study. One process is called the Alpha Process and the other process is called the Beta Process. The primary difference between the two is the different methods used to produce the CO.

A. Alpha Plant Design and Economics.

The basic flow diagram of the Alpha Process is shown in Figure 29. The ground coal is mixed with anthracene oil and enters the reactor with CO where the water-gas shift reaction takes place and coal is reacted to form the tar product. After the reaction, the solids and liquids go to the filters for separation. Since coal hydrogenation plants were first designed, separation by means of filters has always been a problem. But the best concept appears to be: filter the liquids from the solids, then dry the solids in an externally heated kiln to remove the remainder of the liquids and tar.

The liquids (tar and oil) would then go to a distillation unit to separate the anthracene oil from the tar product. In this study, it was assumed that the anthracene oil could be recycled and the same conversion of coal to tar

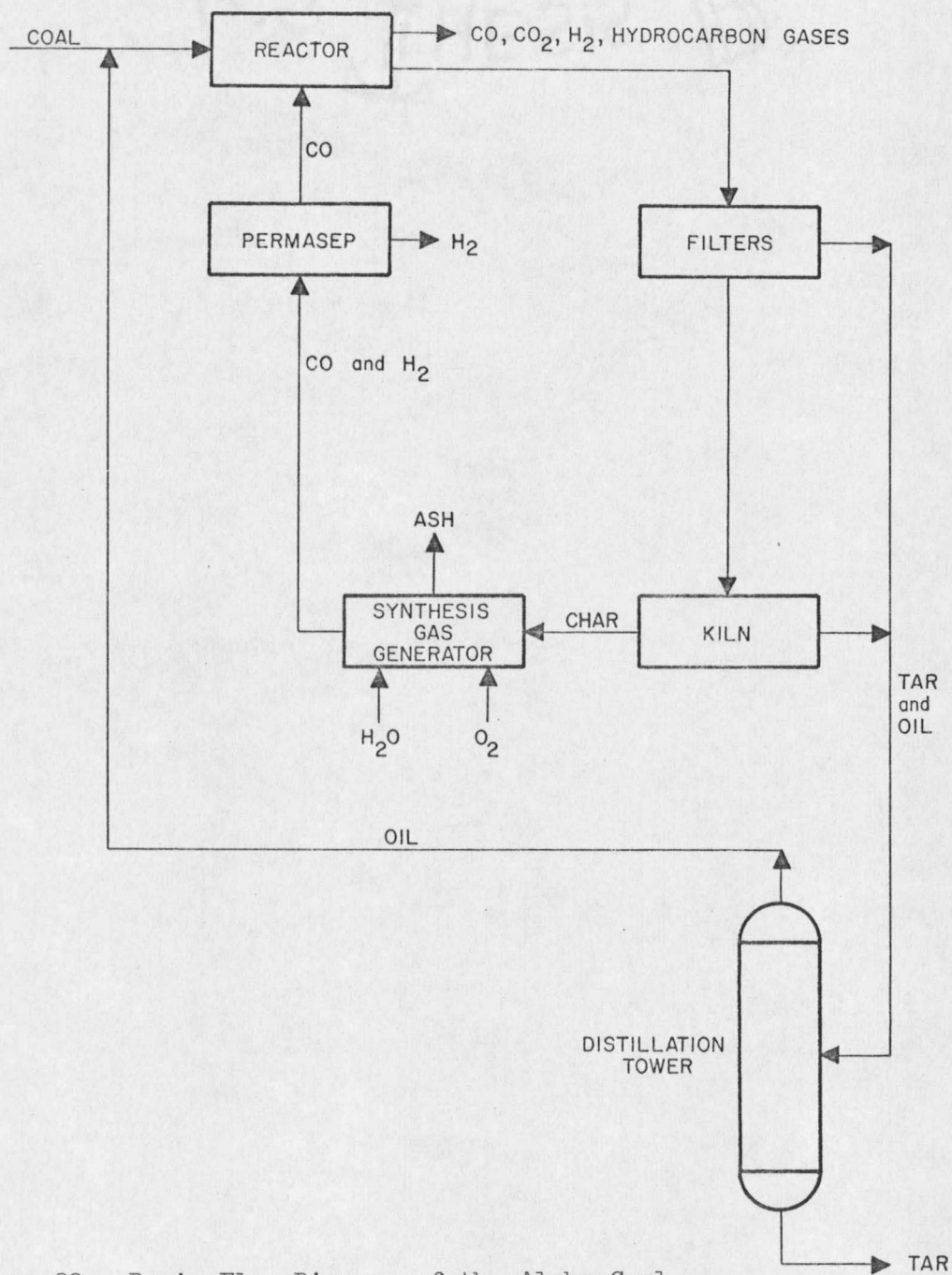


Figure 29. Basic Flow Diagram of the Alpha Coal Liquefaction Process.

could be produced as was found when fresh anthracene oil was used. It is true that anthracene oil is hydrocracked, but it is not very significant even when a hydrogenation catalyst is used (47).

The solids (char) from the kiln would go to the Texaco synthesis gas process for the manufacture of CO (48). In the Texaco Process, char, steam, and oxygen are reacted at about 1000°C to produce CO and H₂ (synthesis gas) and some CO₂ is also produced. Thus an oxygen plant would have to be built to provide the required O₂ for this process.

The CO₂ would be removed from the synthesis gas by using either the Purisol or Rectisol processes (49), and the CO would be enriched to over 95% purity by removing most of the H₂ from the synthesis gas by means of Du Pont's Permasep process (50).

The reaction gases from the reactor would contain many components (i.e. CO, CO₂, H₂, hydrocarbon gases), and it would be very difficult to separate the unreacted CO and recycle it to the reactor. Therefore the reaction gases would be used as a fuel elsewhere in the process; perhaps for the externally heated kiln..

1. Design of the Alpha Process.

A very complete economic study of the Pittsburgh and Midway Process (P&M Process) of producing tar from coal by using hydrogen rather than CO was made under an Office of Coal Research contract (Figure 30). This is the process which was a modification of the old German Pott-Broche Process. In order to make their economic study, they had to design a hypothetical plant based on information that they obtained from a small pilot plant. In many respects the design is similar to the Alpha Process, therefore much of the Pittsburgh and Midway's design and economic data was used for this study. Additional data was needed for the high pressure equipment, and this information was obtained from an economic study of the Consol Process by Consolidation Coal (52).

The basis for the design was the creation of a plant which utilized 10,000 tons of either Noonan lignite or Savage lignite or Colstrip sub-bituminous coal per day for the production of tar. Contrary to Pittsburgh and Midway's economic study, there were to be no by-products such as tar acids, phenol, sulfur, and carbon dioxide in processes used in this study.

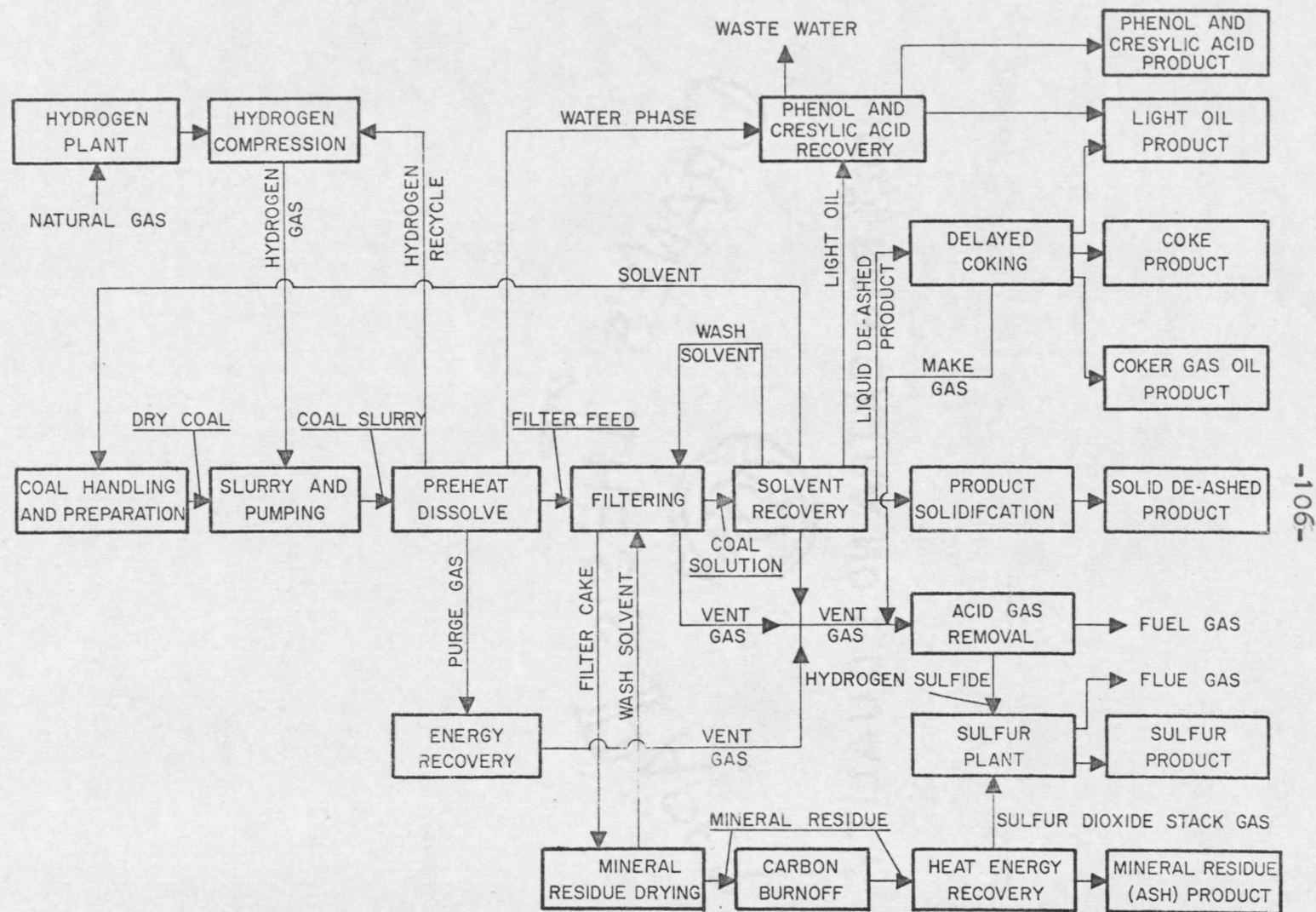


Figure 30. Pittsburgh and Midway Coal Company's Coal Liquefaction Process for the Production of Tar. (51)

In the P&M Process, they relied upon natural gas for their hydrogen, and the char that they produced was used for the production of electricity. The P&M report was felt to be very optimistic. Many large plants with their numerous by-products would saturate the market and result in a reduction of the selling price of these by-products. This would necessitate a considerable increase in the cost of the tar. The advantages of the Alpha and Beta Processes are that there are no by-products and the processes would be self-contained since they use all of the char they produce for the production of CO.

The P&M Process was broken down into 19 basic areas; these are listed in Table XII. Each of these areas was reviewed very carefully and modifications were made to adapt the process to the Alpha Process.

Some comments about certain portions of the plant design are needed. In order to have enough CO for the reactor, 75% conversion must be obtained so that the remaining 25% of the coal will be char which will go into the Texaco process for CO production. Also, for pumping purposes, the ratio of recycle oil to coal (moisture free) in the coal slurry was two to one. If the ratio is much lower, the slurry becomes too viscous to be pumped.

TABLE XII. Capital Cost for the P&M Process by Areas.

<u>Area</u>	<u>Description</u>	<u>Cost</u>
01	Coal Handling and Preparation	
	Coal crushing, screening, drying	\$ 4,228,000
	Coal slurrying and pumping	1,810,000
		6,038,000
02	Dissolver	16,356,000
03	Solid Separation	7,256,000
04	Solvent Recovery	7,817,000
05	Gas Recovery	371,000
06	Mineral Residue Processing	2,097,000
07	Coking Unit	0
08	De-ashed Product Solidification and Storage	3,873,000
09	Power Generation	11,897,000
10	Cooling Water System	1,969,000
11	Waste Water Treatment	1,374,000
12	Tank Farm	363,000
13	Hydrogen Plant	6,300,000
14	Sulfur Plant	4,500,000
15	Acid Gas Removal Plant	2,290,000
16	Phenol and Cresylic Acid Recovery Unit	750,000
17	Instrument and Service Air	110,000
18	Support Buildings	1,380,000
19	Site Preparation	360,000
		\$75,104,000

The CO-to-coal ratio was assumed to be 0.22, or twice the theoretical minimum. From an economic viewpoint, if the ratio is much larger, the size of the reactor needed and the amount of CO required would make the process very impractical. With this CO-to-coal ratio, the reactors' volume which would be needed would be 25,000 ft³ for a residence time of 15 minutes and 100,000 ft³ for a residence time of one hour.

Areas 14 through 16 were not added to the Alpha Process since by-products were not considered in this study. The P&M Process obtained a great deal of sulfur from its coal since it contains about three percent sulfur. The coals used in this study have considerably less sulfur and very little sulfur is removed from the coal. Only small quantities of H₂S are available for making elemental sulfur from Fort Union region coal.

2. Economics of the Alpha Process:

There are many factors in an economic analysis, but these factors can be broken down into four general areas. Factors considered in this report are: cost of coal, operating costs, plant depreciation, and profit. Several different methods allowed by the Internal Revenue Service

can be used to determine plant depreciation. When using straight-line depreciation, the write-off of the plant is the same from year to year. However, there are accelerated depreciations in which the plant write-off is the most rapid during the early years of the plant's operation. Two of the most commonly used methods of accelerated depreciation are the sum-of-the-year's digits method and the double-rate declining-balance method. This report only considered the straight-line and the sum-of-the-year's digits method. The rate of return was calculated by taking the profits and dividing by the investment when straight-line depreciation was used. When the sum-of-the-year's digits method was used, the discounted cash flow method of calculating rate of return was used. In this case both profits and depreciation are considered savings and are invested. The use of this method is described by Kroeger (54).

Three coals (Savage lignite, Noonan lignite, and Colstrip sub-bituminous) were studied using the Alpha Process. In order to obtain 75% conversion, a reactor with one hour residence time had to be used for both Savage lignite and Colstrip sub-bituminous. Since Noonan lignite was much more reactive, a reactor with a 15 minute residence time was considered. The coal cost was assumed to be \$1.50 per

ton whether it be sub-bituminous or lignite coal.

The Alpha Process with Savage lignite requires a plant investment of \$64,000,000, and this cost is itemized according to the 19 sections in Table XIII. The operating costs are based on fuel, manpower, maintenance, property taxes and insurance, and are given in Table XIV. A profit of ten percent was assumed, and Federal taxes were computed at 52.8% of the gross profit.

Using straight-line depreciation, the selling price of the tar (product) would be \$22.74 per ton with 4,250 tons per day being produced. The P&M Process could produce tar from their coal at about \$9.40 per ton, if credits were included. If no credits were included the cost of producing the tar was about \$16.00 per ton (they used the sum-of-the-year's digits method and discounted cash flow). A summary of the costs is shown in Table XV for tar production from Savage lignite using the Alpha Process.

Since some of the tar cost calculations are done by trial and error, when sum-of-the-year's digits method is used along with the discounted cash flow, the calculations become rather long and tedious. Therefore a computer program was used to solve for the annual income required to cover for depreciation, profit, and Federal taxes. A

TABLE XIII. Capital Cost for the Alpha Process Using Savage Lignite.

<u>Area</u>	<u>Description</u>	<u>Cost</u>
01	Coal Handling and Preparation	
	Coal crushing, screening, drying	\$ 2,000,000
	Coal slurring and pumping	4,900,000
		<u>6,900,000</u>
02	Dissolver	21,200,000
03	Solid Separation	5,600,000
04	Solvent Recovery	5,200,000
05	Gas Recovery	0
06	Mineral Residue Processing	4,500,000
07	Coking Unit	0
08	De-ashed Product Solidification and Storage	0
09	Power Generation	2,200,000
10	Cooling Water System	2,000,000
11	Waste Water Treatment	3,800,000
12	Tank Farm	800,000
13	Carbon Monoxide Plant	10,100,000
14	Sulfur Plant	0
15	Acid Gas Removal Plant	0
16	Phenol and Cresylic Acid Recovery Unit	0
17	Instrument and Service Air	100,000
18	Support Buildings	1,400,000
19	Site Preparation	400,000
		<u>\$64,000,000</u>

TABLE XIV. Operating Costs for the Alpha Process Using
Savage Lignite.

<u>Item</u>	<u>Cost (Annual)</u>
Operating Labor (147 men)	\$ 1,220,000
Maintenance	2,360,000
Indirect Labor	340,000
Payroll Overhead	1,300,000
Property Tax and Insurance	1,130,000
Fuel (2,200 MM BTUs per hour @ 10¢ per MM BTUs)	1,900,000
Water	380,000
Catalyst and Chemicals	200,000
Electricity (48,800 KWH @ 5.5¢/KWH)	2,300,000
Interest on Working Capital	400,000
	<u>\$12,000,000</u>

TABLE XV. Cost of Producing Tar from Savage Lignite Using the Alpha Process and Straight-line Depreciation.

Cost of Coal:

$$\begin{aligned} &(\$1.50/\text{ton of coal})(1 \text{ ton of coal}/.565 \text{ tons of organic} \\ &\text{matter})(1 \text{ ton of organic matter}/.74 \text{ tons of tar}) \\ &= \underline{\$3.60} \text{ per ton of tar} \end{aligned}$$

Operating Costs:

$$\begin{aligned} &(\$12,000,000/\text{year})/((10,000 \text{ tons of coal}/\text{year})(.565 \\ &\text{tons of organic matter}/\text{ton of coal})(.74 \text{ tons of tar}/ \\ &\text{ton of organic matter})(360 \text{ operating days}/\text{year}) \\ &= \underline{\$8.00} \text{ per ton of tar} \end{aligned}$$

Depreciation:

$$\frac{(\$64,000,000)(1/20 \text{ years})}{(10,000)(.565)(.74)(360)} = \underline{\$2.12} \text{ per ton of tar}$$

Profit and Federal Tax:

$$\begin{aligned} &\frac{(.10 \text{ profit})(\$64,000,000) \text{ investment}}{(1 - .528 \text{ taxes})(10,000)(.565)(.74)(360)} \\ &= \$9.02 \text{ per ton of tar} \end{aligned}$$

$$\$3.60 + \$8.00 + \$2.12 + 9.02 = \underline{\underline{\$22.74}} \text{ per ton of tar}$$

sample of the calculations is shown in Table XVI. A summary of the cost of producing the tar using the Alpha Process, but switching to the sum-of-the-year's digits method and discounted cash flow shows a decrease in the tar cost (Table XVII)..

In the remainder to the economic studies, the sum-of-the-year's digits method will be used since it is more economically attractive than the straight-line depreciation method is..

If Noonan lignite is used rather than Savage lignite, the only major variable that changes is the reactor size. The decrease in reactor size results in a decrease in the investment cost of the tar production. The cost of producing the tar goes from \$18.58 per ton to \$18.05 per ton.

When Colstrip sub-bituminous is used in the Alpha Process, the cost is reduced considerably simply because there is more organic matter in one ton of sub-bituminous than in lignite. The total plant cost increases from \$64,000,000 to \$66,700,000, but yet the cost of the tar decreases from about \$18.58 to \$15.96, or about the same cost as tar produced by the P&M Process (about \$16.00 per ton). The Alpha Process will produce about 4,900 tons of tar per day when sub-bituminous coal is used..

TABLE XVI. Sample Calculations Using the Sum-of-the-Year's Digits and Discounted Cash Flow.

Investment: \$64,000,000

Rate of Return: 10% DCF

Note: Numbers in Table are Thousands of Dollars

Year	Cash Earnings Before Income Taxes	Deprec- iation	Taxable Income	Income Tax (52.8%)	Net Cash Flow	Discounted Factor (10% at Mid-year)	Present Value
1	10,500	6,125	4,374	2,309	8,190	.953	7,809
2		5,820	4,479	2,470	8,029	.866	6,959
3		5,516	4,983	2,632	7,868	.787	6,200
4		5,211	5,288	2,792	7,707	.716	5,521
5		4,906	5,593	2,953	7,546	.651	4,914
6		4,601	5,898	3,114	7,385	.592	4,372
7		4,297	6,202	3,275	7,224	.538	3,888
8		3,992	6,507	3,436	7,063	.489	3,456
9		3,687	6,812	3,596	6,903	.444	3,070
10		3,382	7,117	3,757	6,742	.404	2,726
11		3,078	7,421	3,928	6,581	.367	2,419
12		2,773	7,726	4,079	6,420	.334	2,146
13		2,468	8,031	4,240	6,259	.303	1,901
14		2,163	8,336	4,401	6,098	.276	1,684
15		1,859	8,640	4,562	5,937	.251	1,490
16		1,554	8,945	4,723	5,776	.228	1,318
17		1,249	9,250	4,884	5,615	.207	1,165
18		944	9,555	5,045	5,454	.188	1,028
19		640	9,860	5,206	5,293	.171	907
20		335	10,164	5,366	5,133	.155	800
		<u>63,781</u>					<u>63,781</u>

TABLE XVII. Cost of Producing Tar from Savage Lignite
Using the Alpha Process and Sum-of-the-Year's
Digits Depreciation Method.

Cost of Coal:

$$\begin{aligned} &(\$1.50/\text{ton of coal})(1 \text{ ton of coal}/.565 \text{ tons of organic} \\ &\text{matter})(1 \text{ ton of organic matter}/.74 \text{ tons of tar}) \\ &= \underline{\$3.60} \text{ per ton of tar} \end{aligned}$$

Operating Costs:

$$\begin{aligned} &(\$12,000,000/\text{year})/(10,000 \text{ tons of coal}/\text{year})(.565 \\ &\text{tons of organic matter}/\text{ton of coal})(.74 \text{ tons of tar}/ \\ &\text{ton of organic matter})(360 \text{ operating days per year}) \\ &= \underline{\$8.00} \text{ per ton of tar} \end{aligned}$$

Depreciation, Profit, and Federal Tax:

$$\frac{(\$10,500,000 \text{ from Table XVI})}{(10,000)(.565)(.74)(360)} = \underline{\$6.98} \text{ per ton of tar}$$

$$\$3.60 + \$8.00 + \$6.98 = \underline{\underline{\$18.58}} \text{ per ton of tar}$$

With one exception, the P&M Process is slightly cheaper than the Alpha Process, but yet the experimental work in this study and in others show that the water-gas shift reaction should definitely be better. Where is the discrepancy? The P&M Process uses 1,000 psi pressure and 15 minutes residence time for the reactor, which is a much lower pressure than the 5,000 psi used in the Alpha plant design. This indicated that the conversions obtained in the rocking autoclave are very low, thereby giving us very conservative results. Also, the P&M Process uses a higher grade coal (an Appalachian bituminous) and more organic material is found in this coal than is in lignite and sub-bituminous coals.

B. Beta Plant Design and Economics.

The basic flow diagram of the Beta Process is shown in Figure 31. The production of the tar from the coal, the separation of solids from the tar and oil, and the separation of the tar from the recycle oil is the same as seen in the Alpha Process.

The difference in this process is in the production of CO, and in the utilization of the tar. The tar in this process is used specifically for MHD, since heat from the

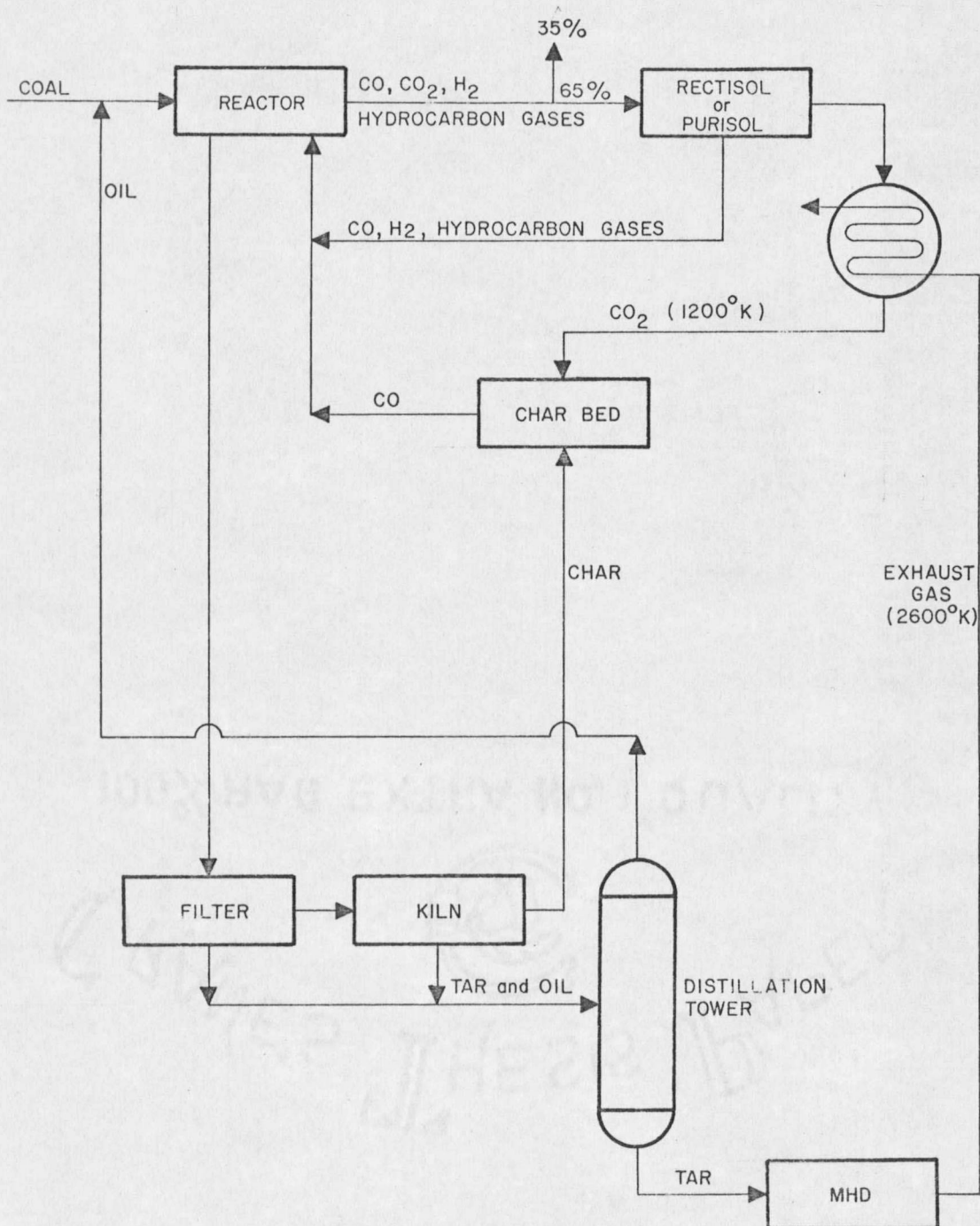


Figure 31. Basic Flow Diagram of the Beta Coal Liquefaction Process.

2,600°K exhaust gas from MHD will be used to produce the CO.

The gases from the reactor contain CO, CO₂, H₂, and hydrocarbon gases. The CO₂ will react with the carbon in the char at temperatures above 1,200°K resulting in essentially pure CO (55,56). In order to obtain a balance so that no excess char exists, there must be at least 87% conversion, and 65% of the reaction gases must be recycled in order to have enough CO₂ for the production of CO. In order to prevent an accumulation of H₂ and the undesirable gases, the remaining 35% of the reaction gas is passed out of the reactor as a fuel.

1. Design of the Beta Process:

The same basic design criteria applies to the Beta Process as is seen in the Alpha Process. In this study, only Noonan lignite and Colstrip sub-bituminous with Na₂CO₃ were used since they were the only coals which would yield 87% conversion in one hour reaction time.

2. Economics of the Beta Process:

The same general procedure is used to make the economic study in the Beta Process as was used in the Alpha Process. Again, the sum-of-the-year's digits and discounted cash flow will be used in this study.

If Noonan lignite is used in the Beta Process the cost of the tar is now reduced from \$18.05 per ton (in the Alpha Process) to \$14.94 per ton. The decrease in cost is attributed to a higher conversion of the coal to tar, and to a more efficient process of producing the CO. The Beta Process, using Colstrip sub-bituminous, reduces the cost from \$15.96 per ton to \$13.78 per ton. A summary of the costs using sub-bituminous in the Beta Process is shown in Table XVIII.

It may be easier for the reader to compare the cost of tar if other units are used. The \$13.78 per ton corresponds to about \$2.40 per barrel, or 42.9 cents per million BTUs.

C. Changes in Economic Variables.

All of the variables in the previous discussion were fixed. It is the purpose of this section to investigate the effects of the more important variables on the cost of producing the tar product. Figures 32, 33, 34, and 35 show the effects of changing coal costs, plant costs, operating costs, and rates of return on the cost of the tar product. The Beta Process using Colstrip sub-bituminous will be used as an example.

From Figure 32 we see that a change in the operating

TABLE XVIII. Cost of Producing Tar from Colstrip Sub-bituminous Using the Beta Process.

Cost of Coal:	\$ 2.67 per ton of tar
Operating Cost:	6.21 per ton of tar
Depreciation, Federal Taxes, and Profit:	<u>4.90</u> per ton of tar
	\$13.78 per ton of tar

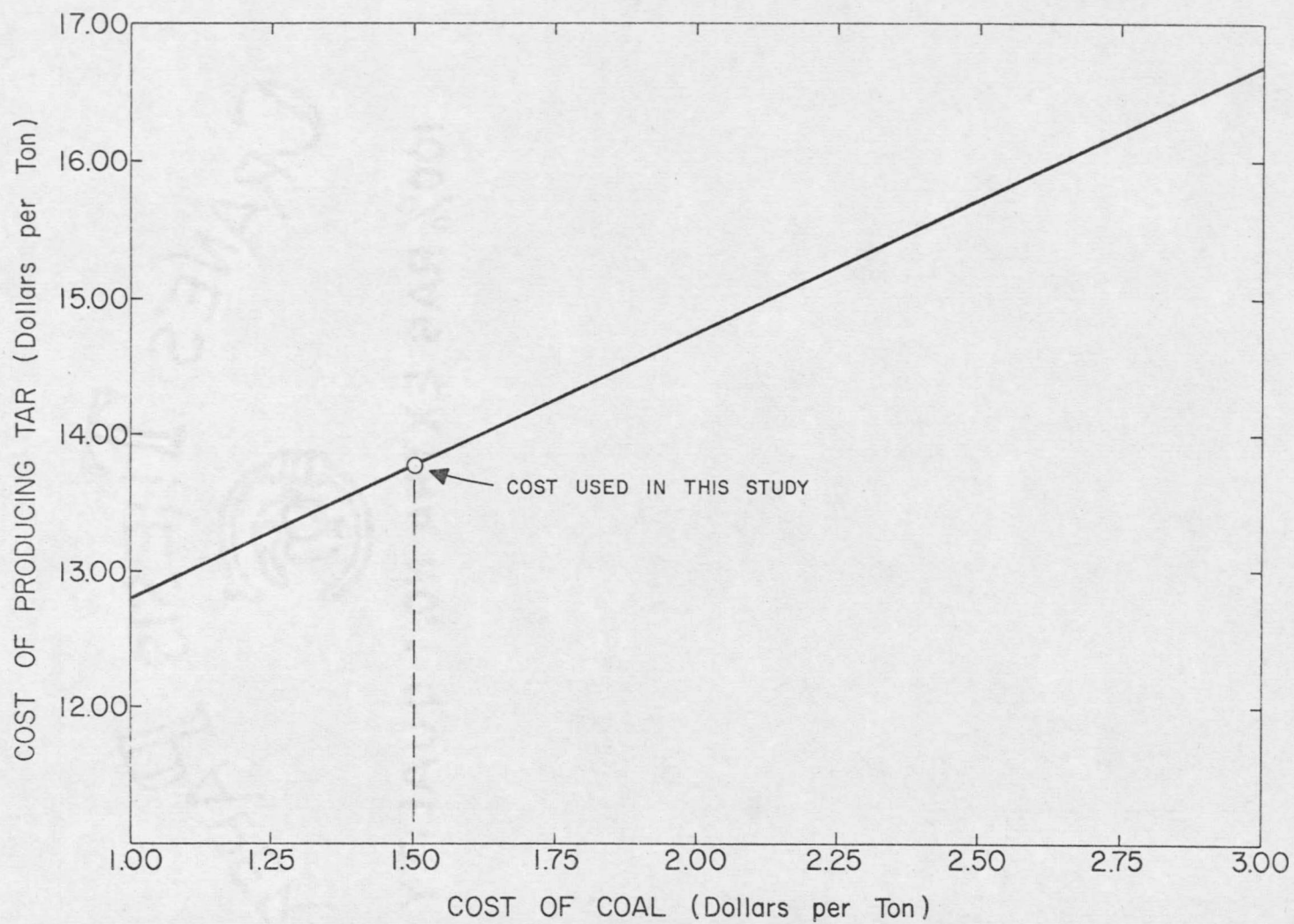


Figure 32. Effect of the Cost of Coal on the Cost of Producing Tar from the Beta Process.

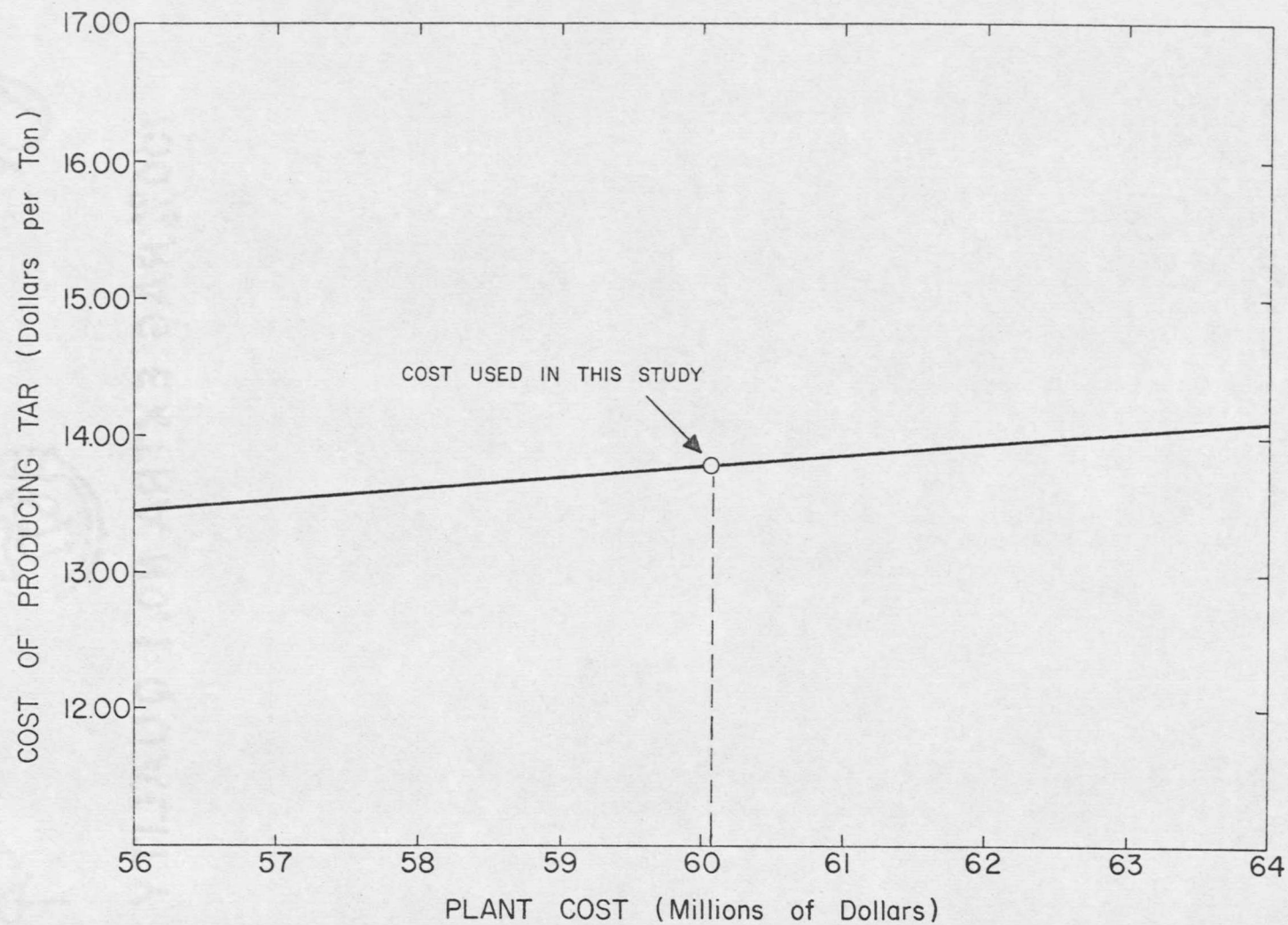


Figure 33. Effect of the Plant Cost on the Cost of Producing Tar from the Beta Process.

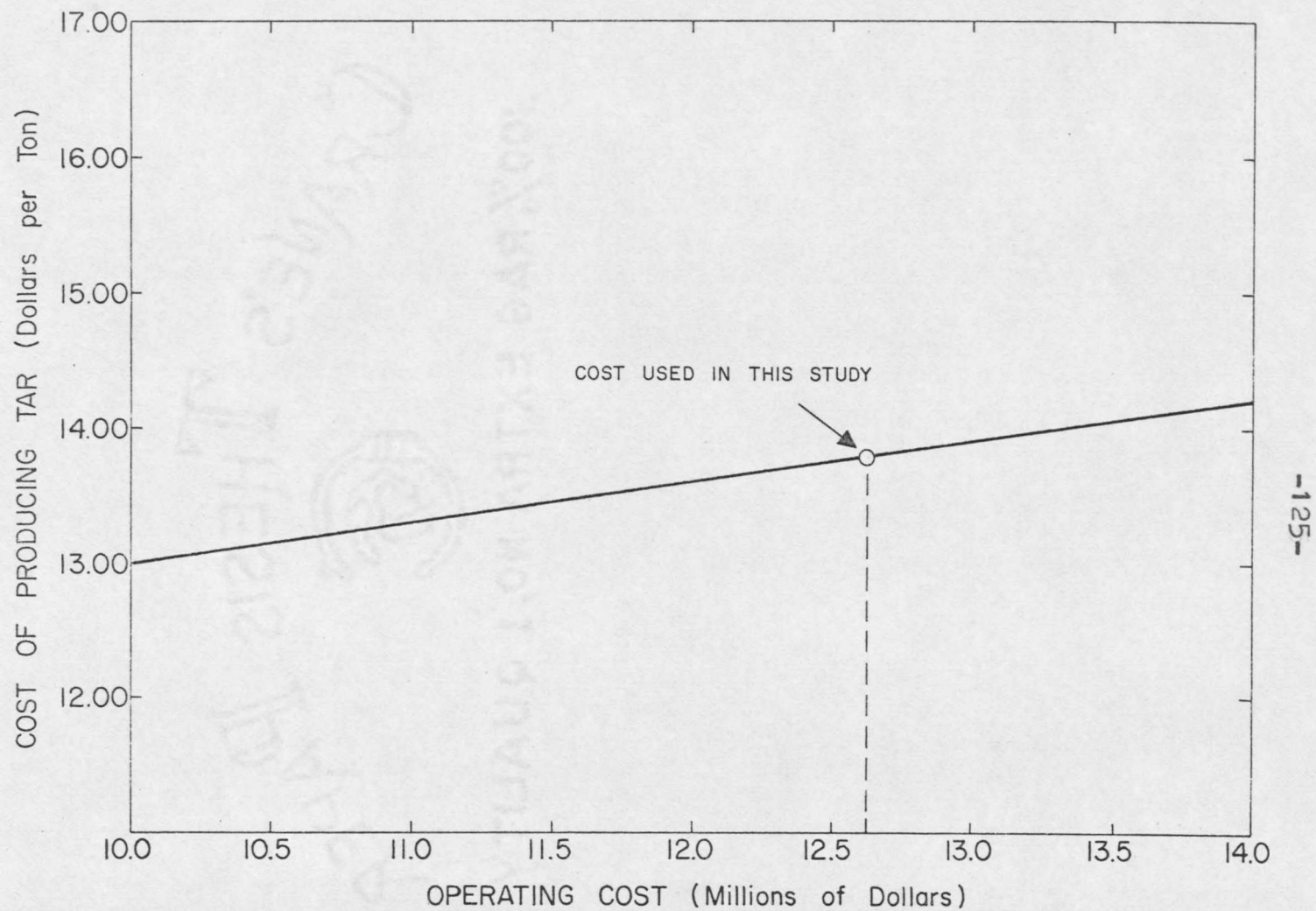


Figure 34. Effect of the Operating Cost on the Cost of Producing Tar from the Beta Process.

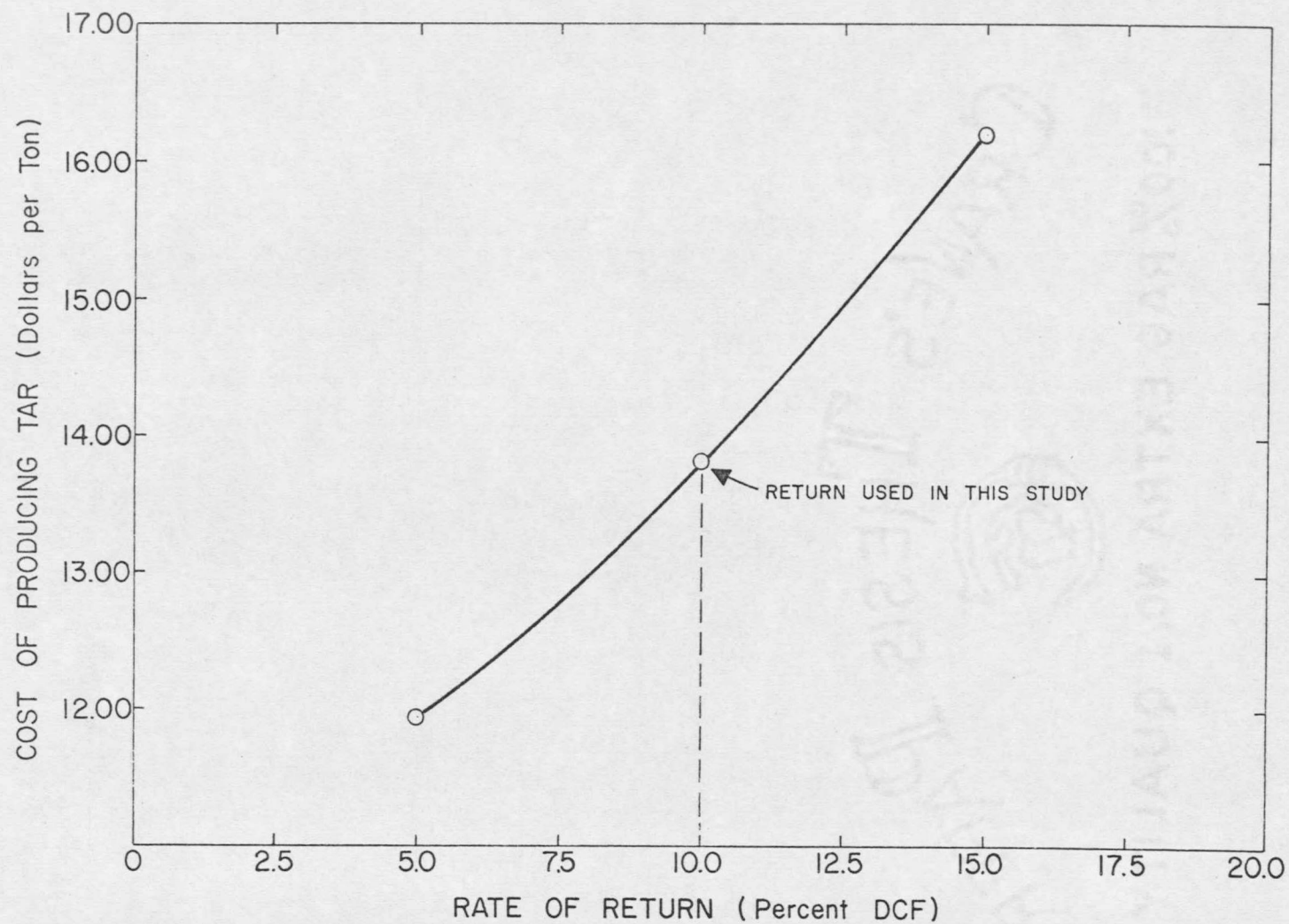


Figure 35. Effect of Rate of Return on the Cost of Producing Tar from the Beta Process.

cost does not constitute a great change in the cost of tar production. For example, a reduction of \$2,000,000 in annual operating costs would reduce the cost of the tar from \$13.78 to about \$13.45. Also, the reduction of the plant costs has even less effect on the total cost of the tar (Figure 33).

The future cost of coal is a very important factor, and this cost could range from \$1.00 per ton to as high as \$2.50 per ton. Rate of return is a very important variable in the production cost of the tar. For example, if a rate of return of 5% is desired, the production cost of the tar would be about \$12.00 per ton. If a rate of return of 15% is desired, the production cost of the tar would be about \$16.00 per ton.

From a technological standpoint, the variables of operating costs and plant costs (capital) are the most influential to a process' success, but in this case they change the economics less than coal cost and rate of return. Therefore, this rough economic estimate should be fairly accurate. It was found that major modifications or a great number of minor modifications will have to be made to significantly change the cost of producing the tar.

VII. CONCLUSIONS

The supporting research, which consisted of experimental runs using the water-gas shift reaction on coal produced the following major conclusions:

(1) Increasing operating pressure will increase the conversion of the coal to a benzene soluble material.

(2) Increased temperature increases conversion, but the hydrocarbon gas production also increases.

(3) There appears to be sufficient water in the coal to obtain maximum conversion without adding additional water, particularly for a commercial reactor.

(4) The effective solvents for conversion of sub-bituminous coal in decreasing order are: isoquinoline, anthracene oil, ANP, no solvent, and tar. For lignite the order is: ANP, isoquinoline, and anthracene oil.

(5) The more grinding that is done to the coal, the less the conversion. This is probably caused by aging of the coal taking place during the drying and grinding processes (oxidation).

(6) When tested using the same conditions, the four coals studied all gave different conversions and it is believed that the sodium in the coal accounts for these

differences.

(7) The gas analyses show that the water gas shift reaction is more complete toward equilibrium when conversion is greater.

(8) The liquefied product from the coal has an ash content of less than 0.1% and a hydrogen-to-carbon ratio of about 1.14. The product has a molecular weight of about 400 and looks very much like a tar. The char product has an ash content of about 29% and a hydrogen-to-carbon ratio of about 0.70.

(9) In most cases when Na_2CO_3 was added to the coal, conversions increased by at least 10%.

(10) The results of runs using several different organic materials (asphalt, cellulose) show that the quantity and quality of the ash has a very strong influence in catalyzing the water-gas shift reaction.

Information was obtained to indicate why CO plus water works more effectively in converting coal to liquid products than is seen when hydrogen is used. The sodium and iron in the coal act as catalysts for the water-gas shift reaction thereby producing nascent hydrogen. This reactive hydrogen then stabilizes the reactive fragments produced from the thermal depolymerization of the coal.

With the aid of the supporting research and through the use of existing, proven processes, the primary objective of this research project was met. Two coal liquefaction processes were developed which utilized Fort Union region coal and incorporated the water-gas shift reaction on the coal. The important contributions of these processes are that they eliminate the costly process of producing hydrogen in a separate step, and there is no char produced as a by-product in the process. One of the processes (Alpha) which produced tar from coal was competitive with existing coal reduction processes using hydrogen. It is important to point out that the economic studies were done on a very conservative basis and that it is quite possible that the Alpha Process would be even more economically attractive than the existing processes. The second process which produced tar for MHD is definitely more economically attractive than the Alpha Process.

The use of the tar product from these processes as a MHD fuel will overcome many of the obstacles that have prevented MHD from becoming a reality. If this fuel does indeed make MHD a reality, it will help immensely in solving the United States' energy problems.

VIII. RECOMMENDATIONS FOR FUTURE STUDY

(1) Future study should begin with an investigation with an institution interested in MHD to see precisely what the production of tar from coal using the Beta Process will do to the economics of the MHD system.

(2) It is felt that the processes proposed in this study should at least be studied with a continuous reactor so that the effects of mixing, reactor size, and operating conditions could accurately be determined. Also, a small pilot plant should be built to investigate the entire process. This is a very expensive procedure and requires personnel experienced in high pressure technology. A pilot plant necessary to make this study would cost at least \$150,000 plus operating expenses.

(3) Ways of mutually improving both the MHD system and the coal liquefaction process should be investigated. For example, since it does have an important effect on MHD, the hydrogen-to-carbon ratio as a function of the operating variables in the reactor should be investigated.

(4) There are many other studies that could be made using the rocking autoclave. This could include investigation of coal particle size, ratio of solvent to coal, and

the interreaction of pressure and solvent on conversion..

(5) The use of gases other than pure CO would be well worth investigating since an industrial plant would not be expected to produce pure CO. Some gas mixtures could include mixtures of CO, H₂, CO₂, and the hydrocarbon gases..

(6) A catalyst needing investigation which may be cheaper and produce better results than Na₂CO₃ is the waste product from the alumina process called "red mud." This typically consists of Fe₂O₃, 40.8%; Al₂O₃, 15.2%; SiO₂, 9.8%; TiO₂, 5.8%; Na₂O, 9.3%; CaO, 4.1%; P₂O₅, 1.3% (57).

(7) By-products could be valuable in reducing the cost of the tar produced from the coal. For example, the production of the tar acids, phenol, sulfur, and ammonia should be studied.

(8) Using the water-gas shift reaction on coal as a means of removing sulfur from high-sulfur coals would be worth investigation. This would be of value since it may be a way of reducing air pollution in steam generating plants..

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IX.. APPENDIX

Example of Detailed Calculations of a Plant Design and Economics Using the Alpha Process with Savage, Montana Lignite.

The basis of the design is 10,000 tons of coal per day, or $(10,000 \text{ tons per day})(2000 \text{ lbs/ton})(\text{day}/24 \text{ hours}) = 833,000 \text{ lbs/hour}$. The proximate analysis for Savage lignite is: 36.0% water, 7.5% ash, and 56.5% organic matter, therefore the rate of water, ash, and organic matter the plant is $(833,000 \text{ lbs of coal/hour})(.360) = 300,000 \text{ lbs of water per hour}$, $(833,000 \text{ lbs of coal/hour})(.075) = 63,000 \text{ lbs of ash per hour}$, and $(833,000 \text{ lbs of coal/hour})(.565) = 470,000 \text{ lbs of organic matter per hour}$. The ratio of solvent to coal, on a water-free basis is 2 to 1, therefore $2(470,000 + 63,000) = 1,066,000 \text{ lbs of solvent per hour}$.

A stoichiometric balance of the carbon in the plant must be made so that enough CO is available to convert coal to tar. First it would be desirable to know how much of the carbon in the char goes to CO in the Texaco synthesis gas process. The char that the IGT gasification process produces is quite different than the char we obtained; however, for the lack of anything better, we went ahead and used the IGT char as a basis for the calculations (Table

TABLE XIX: Stoichiometric Balance of the Texaco Synthesis Gas Production Process Using IGT Char.

Analysis of the IGT char:

<u>element</u>	<u>weight percent</u>	<u>lbs/hour</u>
C	76.25	306,977
H	1.77	7,125
O	1.55	6,246
N	0.52	2,016
S	0.11	440
ash	15.80	79,684

Additional material needed to make synthesis gas:

O ₂	317,312
H ₂ O	241,603
total	961,413

The output streams will consist of:

<u>Component</u>	<u>mole percent</u>	<u>moles/hour</u>	<u>lbs/hour</u>
CO	47.20	19,086	534,618
CO ₂	10.57	4,274	188,103
H ₂	27.24	11,013	22,202
N ₂	0.18	72	2,016
Ar	0.10	43	1,718
CH ₄	0.12	48	770
H ₂ S	0.04	16	544
H ₂ O	14.55	5,883	105,988

The residue will consist of:

	<u>weight percent</u>	<u>lbs/hour</u>
C	24.49	25,828
ash	75.51	79,628
Total		961,413

XIX). The percent of the carbon in the char going to CO is: 19,086 moles of CO/hour contains 19,086 moles of C/hr, and $(19,086 \text{ moles of C/hour})(12 \text{ lbs/lb mole}) = 228,000 \text{ lbs of C per hour in the CO.}$ $(228,000 \text{ lbs of C in CO})(307,000 \text{ lbs of C in char})(100\%) = 74.5\%$ of the C in the char goes to CO.

Now we must find out what conversion is required to have a carbon balance. This was a trial and error computation, and only the final results will be given. Assume 75% conversion of the coal to tar and gas. The hydrogen-to-carbon ratio for the gases produced from the coal is 3.0 and 3% of the coal goes to these hydrocarbon gases. The hydrogen-to-carbon ratio for the tar product is 1.1 and 74.7% of the coal goes to the tar. The hydrogen-to-carbon ratio for the char is 0.7 and 25% of the coal goes to char, therefore the carbon-to-hydrogen ratio for all of the reaction products would be approximately: $(3.0)(.003) + (1.1)(.747) + (0.7)(.250) = 1.006$. The hydrogen-to-carbon ratio for the original coal was 0.83, therefore the increase in the hydrogen-to-carbon ratio would be $(1.01 - 0.83) = 0.18$. The coal contains 42.2% carbon, therefore 30 grams of Savage lignite would contain 12.68 grams of carbon or 1.05 gram moles of carbon. Thus, the amount of hydrogen

required to give 75% conversion would be: $(1.05 \text{ g-moles carbon})(0.18) = 0.19 \text{ g-moles hydrogen}$, which is equivalent to $0.095 \text{ g-moles of } H_2$. If we double the amount of hydrogen that will be potentially available, then we must have $2(0.095)$, or $0.19 \text{ g-moles of } H_2$. From the equation $CO + H_2O \rightarrow H_2 + CO_2$, we must then manufacture $0.19 \text{ g-moles of } CO$.

Next, we must see if enough carbon in the char is available to produce the required amount of CO. It is shown that $(1.05 \text{ g-moles of C})(0.25) = 0.26 \text{ g-moles of carbon in the char}$, or $(.26)(.745) = 0.197 \text{ g-moles of CO}$ is available, which will supply the $0.19 \text{ g-moles of CO}$ that is required.

Each section of the Pittsburgh and Midway coal liquefaction process will be reviewed, and adjusted to give a cost estimate of our Alpha Process.

Area 01 - Coal Handling and Preparation (coal crushing, screening, drying). The cyclones and flash dryers were removed from the P&M Process because it is undesirable to remove the water from the coal. The crushing and screening equipment were left as they were designed, but conveyors and other auxiliary equipment for the dryers were removed. The P&M Process cost of \$4,200,000 less the cost of the

drying equipment. (\$2,200,000) gives an Alpha Process cost of \$2,000,000.

Area 01 - Coal Handling and Preparation (coal slurring and pumping). It was very difficult to find cost estimates on pumps which will pump a slurry, so the 0.8 power factor rule was used. The P&M process pumped 2,500,000 pounds of slurry per hour to 1000 psi, while the Alpha process pumps 1,900,000 pounds of slurry per hour to 5000 psi. The slurry pumps in the P&M process cost \$1,600,00, therefore the Alpha process pumps are estimated to cost (\$1,600,000) $(5000/1000)^{0.8} (1,900,000/2,500,000)^{0.8} = \$4,700,000$. The remaining heat exchangers and other vessels would have about the same cost of \$200,000, or the cost of this section of the plant would be \$4,700,000 + \$200,000 = \$4,900,000. The total cost of Area 01 is \$2,000,000 + \$4,900,000 = \$6,900,000.

Area 02 - Dissolver. First the volume of the reactor must be determined before the cost can be calculated. The volume of coal for a 1 hour residence time in the reactor is: $(533,000 \text{ lbs/hour of moisture free coal}) (1/62.4 \text{ lbs/ft}^3) (1/\text{density of } 1.5) = 5,600 \text{ ft}^3$. The volume of water for a 1 hour residence time is: $(300,000 \text{ lbs/hour}) (1\text{-moles}/18 \text{ lbs}) = 16,560 \text{ lb-moles H}_2\text{O}$, or $V = nRT/P =$

$(16,560 \text{ lb-moles})(.730)(1290^{\circ}\text{R})(14.7 \text{ psi/atm})/(5000 \text{ psi}) = 47,200 \text{ ft}^3$. The volume of CO for a 1 hour residence time is: $0.19 \text{ g-moles CO}/30 \text{ grams of coal} = 0.0063$, or $.0063 (833,000 \text{ lbs of coal/hour}) = 5,240 \text{ lb-moles of CO}$ which corresponds to $14,800 \text{ ft}^3$ of CO. The volume of solvent for a 1 hour residence time is $(1,066,000 \text{ lbs/hour})(\text{ft}^3/62.4 \text{ lbs})(1/\text{density of } 0.9) = 19,000 \text{ ft}^3$. Thus the total volume of the reactor would be: $5,600 + 47,200 + 14,800 + 19,000 = 86,600 \text{ ft}^3$.

The Consolidation Consol Process used a series of reactors which had a total volume of $170,000 \text{ ft}^3$ at a cost of \$10,200,000, therefore the cost of the 5000 psi reactors for the Alpha Process would be: $(87,000/170,000)^{0.8} (\$10,200,000) = \$6,000,000$. The value of the remaining equipment in the dissolver section was assumed to be: heat exchangers, \$2,400,000; vessels, \$1,200,000; fired heaters, \$10,000,000; compressors, \$1,500,000 for a total cost of Area 02 of \$21,200,000.

Area 03 - Solid Separation. The amount of solvent to be separated is less than in the P&M Process. The total amount of material to be separated in the P&M Process is 2,500,000 lbs/hour, at a cost of \$7,300,000. The total amount of material to be separated in the Alpha Process

is 1,900,000 lbs/hour, or $(\$7,300,000)(1,900,000/2,500,000)^{0.8} = \$5,600,000.$

Area 04- Solvent Recovery. The amount of tar and solvent to be separated in the Alpha Process is considerably less than in the P&M Process which cost \$7,800,000. By again using the 0.8 power factor rule, the cost of the area in the Alpha Process is $(((.75 \text{ conversion})(470,000) + 1,066,000)/((.90 \text{ conversion})(750,000) + 1,667,000))^{0.8} (\$7,800,000) = \$5,200,000.$

Area 05 - Gas Recovery. In the Alpha Process there was no gas recovery.

Area 06 - Mineral Residue Processing. The production of char from the Alpha Process is considerably greater than in the P&M Process which cost \$2,100,000. Therefore, the cost of the Alpha Process mineral residue processing would be $((2(.25)(470,000)/(90,000))^{0.8} (\$2,100,000) = \$4,500,000.$ The factor 2 on the numerator was added because the Alpha Process product is considered to be quite heavy, thereby requiring a large amount of the tar to be removed in this step.

Area 07 - Coking Unit. There was no coking unit in the Alpha Process.

Area 08 - De-ashed Product Solidification and Storage.

There was no solidification and solid storage in the Alpha Process.

Area 09 - Power Generation.. In the P&M Process, the char was used for the generation of electricity. In the Alpha Process, the char is all used for the production of CO, although some steam boilers will be required for the Alpha Process. Thus, all of the of the turbine generators and mineral residue fuel boilers were removed. This reduced the power generation area from \$11,900,000 to no more than \$2,200,000.

Area 10 - Cooling Water System. There did not appear to be any significant differences between the Alpha and P&M Processes, so the same figure as was derived from the P&M study was used (\$2,000,000).

Area 11 - Waste Water Treatment.. This part of the process was probably the most difficult one to obtain an estimate on since it is not known what happens to most of the reaction water in the M&P Process. The Alpha Process has considerably more reaction water than the P&M Process, but most of it probably would not have to go through a treatment. It was therefore assumed that a waste water treatment plant three times the size of the one in the P&M Process would be adequate. Thus, $(3)^{0.8}(\$1,400,000) =$

\$3,800,000.

Area 12 - Tank Farm. The size of the tank farm was doubled in the Alpha Process from what was called for in the P&M Process, or a cost of \$800,000.

Area 13 - CO Generation. The cost estimate for this part of the study came from the IGT study on a coal gasification process. In the IGT process, they processed 402,000 lbs of char per hour and the capital cost was \$7,500,000, therefore our cost would be: $((.25)(470,000)/(402,000))^{0.8}(\$7,500,000) = \$2,800,000$. The CO₂ removal is included in this cost, however, the removal of the H₂ had to be done by using the design data given by Du Pont, and the cost of hydrogen removal to obtain 96% CO would cost approximately \$700,000.

The oxygen plant for the oxygen required for generation of synthesis gas was also obtained from the IGT report. Calculations for the oxygen plant costs were done in the same manner as the cost of the synthesis gas generator: $((.25)(470,000)/(402,000))^{0.8}(\$9,400,000) = \$7,300,000$, or the total cost of CO generation is $\$2,800,000 + \$7,300,000 = \$10,800,000$.

Area 14 - Sulfur Plant. There was no sulfur plant in the Alpha Process.

Area 15 - Acid Gas Removal Plant. There was no acid gas removal plant in the Alpha Process.

Area 16 - Phenol and Cresylic Acid Recovery Unit. There was no phenol and cresylic acid recovery unit in the Alpha Process.

Area 17 - Instrument and Service Air. The instrument and service air were assumed to cost the same in the Alpha Process as in the P&M Process, or \$100,000.

Area 18 - Support Buildings. The cost of the support buildings was assumed to cost the same in the Alpha Process as in the P&M Process, or \$1,400,000.

Area 19 - Site Preparation. The cost of the site preparation was assumed to cost the same in the Alpha Process as in the P&M Process, or \$400,000.

A summary as to how the operating costs were obtained will be given. Table XX shows the areas which consume the greatest amounts of heat and electricity.

The reaction gases from the reactor has a heating value of about only 100 MM. BTU/ hour if the exhaust reaction gases are assumed to contain 327 lb-moles of H_2 , and 327 lb-moles of CO, along with some hydrocarbon gases. Also some hydrogen could be used as fuel which was produced in the CO purification step, and this would yield about 400

TABLE XX. Heat and Electrical Requirements for the Alpha Process Using Savage, Montana Lignite.

A. Heating Requirements by Areas.

<u>Area</u>	<u>Description</u>	<u>Consumption (MM BTU/hour)</u>
02	Dissolver preheater	1,500
04	Vacuum flash heater	300
04	Wash solvent heater	300
06	Mineral dryers	100
09	Power generation	100
13	CO generation	<u>400</u>
	Total consumption	2,700

B. Electrical Requirements by Areas.

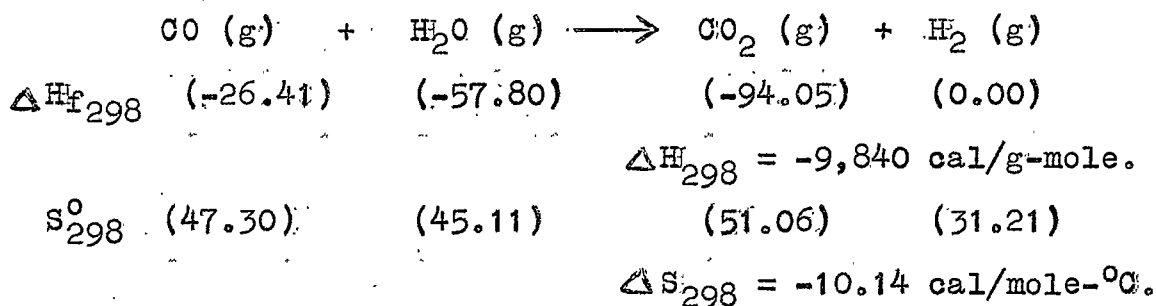
<u>Area</u>	<u>Description</u>	<u>Consumption (KWH)</u>
01	Grinding, conveyors	20,000
02	Pumping, compression	3,500
03	Filtration	1,300
04	Pumping	1,400
06	Rotary kilns	400
10	Pumping, cooling fans	3,200
11	Pumping	600
13	Oxygen plant	17,200
17	Compressors	200
	Miscellaneous	<u>1,000</u>
	Total requirements	48,800

MM BTU/hour of heat, therefore the total amount of heat required would be: $2,700 - 100 - 400 = 2,200$ MM BTU/hour.

The manpower requirements were calculated from the P&M report and the subtraction of manpower in the sulfur plant and phenol plant were considered. Also, the additions of men in the oxygen plant were considered. The P&M process required 155 men, and the Alpha Process would require 147 men.

The Thermodynamic Chemical Equilibrium Calculations for The Water-gas Shift Reaction.

The water-gas shift reaction and the changes in entropy and enthalpy are given as:



The equilibrium constants for the reaction have been determined by Rossini (58), and are as follows:

<u>Temperature ($^\circ\text{C}$)</u>	<u>K_{eq}</u>
27	9.01×10^4
127	1.48×10^3
227	1.32×10^2
327	27.1
427	9.01
627	2.11
827	0.949
1027	0.547

To determine what the conversion of the water-gas gas shift reaction is at the conditions we were operating at, the equation $K_N = P^{\Delta n} K_{eq} / K_y$ is used, but $\Delta n = 0$, and K_y is found by using the equation $K_y = \gamma_{\text{CO}_2} \gamma_{\text{H}_2} / \gamma_{\text{CO}} \gamma_{\text{H}_2\text{O}}$. γ is found by using the equation $\ln \gamma = (9PT_c / 128P_c T) (1 - 6(T_c^2 / T^2))$, where Δn is the change in the number of moles

in the reaction, P is the pressure, P_c is the critical pressure, T is the temperature, T_c is the critical temperature, γ is the activity coefficients, and K_N is the equilibrium constant.

The critical pressures and temperatures for the gases being studied are:

	<u>CO</u>	<u>H₂O</u>	<u>CO₂</u>	<u>H₂</u>
P_c	34.5 atm	218 atm	72.9 atm	12.8 atm
T_c	133°K	647°K	304°K	33.3°K

The equilibrium constant in terms of the change in the number of moles is:

	<u>CO</u>	+	<u>H₂O</u>	→	<u>CO₂</u>	+	<u>H₂</u>
at start	1		1		0		0
at equil.	(1-x)		(1-x)		x		x

and the total relative number of moles at equilibrium is 2, therefore $K_N = (x/(1-x))^2$. Thus by using the equation $(x/(1-x))^2 = K_{eq}/K_\gamma$, the final results are obtained:

<u>Pressure</u>	<u>Temperature</u>	<u>K_γ</u>	<u>K_N</u>	<u>% conversion</u>
300 atm	327°K	1.72	15.8	79.8
	427	1.39	6.49	71.9
	627	1.17	1.89	57.9
400 atm	327°K	2.06	13.2	78.5
	427	1.56	5.78	70.6
	627	1.23	1.80	57.4

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