



The design and preliminary optimization of a continuous coal liquefaction system utilizing a coiled tubular reactor
by Michael John Biegelke

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE
in Chemical Engineering
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Abstract:

A coiled tubular reactor was developed for the rapid hydrogenation of coal. Operational problems of feeding the coal to the system were solved.

The coal studied was a sub-bituminous coal from Colstrip, Montana. The effects of various variables which existed in the equipment, namely temperature, pressure, hydrogen flowrate, reactor length, and catalysts, were studied for their effect on coal conversion.

Three catalysts were studied: nickel chloride, stannous chloride, and stannic chloride. Two methods of catalysis were studied—impregnation of the catalyst and mixing the catalyst with the coal.

The results showed that increasing pressure and temperature increased conversion. Conversion decreased with increasing hydrogen flowrate. Reactor length and coal feedrate did not have any significant effect on coal conversion in the ranges tested. The highest coal conversion (48.0%) was obtained with impregnated stannous chloride (13.9%). Next best conversions were obtained with nickel chloride and stannic chloride, in that order.

Impregnating the catalyst on the coal produced higher conversions (for each respective catalyst) than did mixing the catalyst with the coal. Differences ranged from 5.1% for stannic chloride to 7.0% nickel chloride.

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THE DESIGN AND PRELIMINARY OPTIMIZATION OF A CONTINUOUS COAL
LIQUEFACTION SYSTEM UTILIZING A COILED TUBULAR REACTOR

by

MICHAEL JAMES BIEGALKE

A thesis submitted in partial fulfillment
of the requirements for the degree

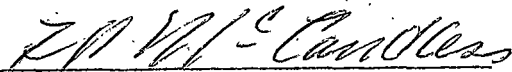
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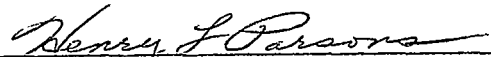
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ABSTRACT

A coiled tubular reactor was developed for the rapid hydrogenation of coal. Operational problems of feeding the coal to the system were solved.

The coal studied was a sub-bituminous coal from Colstrip, Montana. The effects of various variables which existed in the equipment, namely temperature, pressure, hydrogen flowrate, reactor length, and catalysts, were studied for their effect on coal conversion. Three catalysts were studied: nickel chloride, stannous chloride, and stannic chloride. Two methods of catalysis were studied--impregnation of the catalyst and mixing the catalyst with the coal.

The results showed that increasing pressure and temperature increased conversion. Conversion decreased with increasing hydrogen flowrate. Reactor length and coal feedrate did not have any significant effect on coal conversion in the ranges tested. The highest coal conversion (48.0%) was obtained with impregnated stannous chloride (13.9%). Next best conversions were obtained with nickel chloride and stannic chloride, in that order.

Impregnating the catalyst on the coal produced higher conversions (for each respective catalyst) than did mixing the catalyst with the coal. Differences ranged from 5.1% for stannic chloride to 7.0% nickel chloride.

INTRODUCTION

A. Current United States Energy Situation

As the world becomes more dependent upon the Middle Eastern countries for the supply of petroleum, the search for alternative energy sources becomes more and more intense. The United States is also faced with the problem of decreasing national petroleum production. This is a critical matter to this country as it is one of the most energy intensive countries in the world. The supply of petroleum not only affects the standard of living for its citizens, but is also a major factor in determining the position of a country in the world economic picture as well as determining the national economic picture. The disadvantageous position of the United States in terms of both international and national economic situations is shown by the negative balance of trade with foreign countries. A large percentage of this negative balance is a result of the importation of petroleum from the Middle East. Thus, it is seen that in order for the United States to remain a world power, to maintain a high standard of living for its citizens, and to maintain its economic independence, it is necessary for the United States to define alternative energy sources.

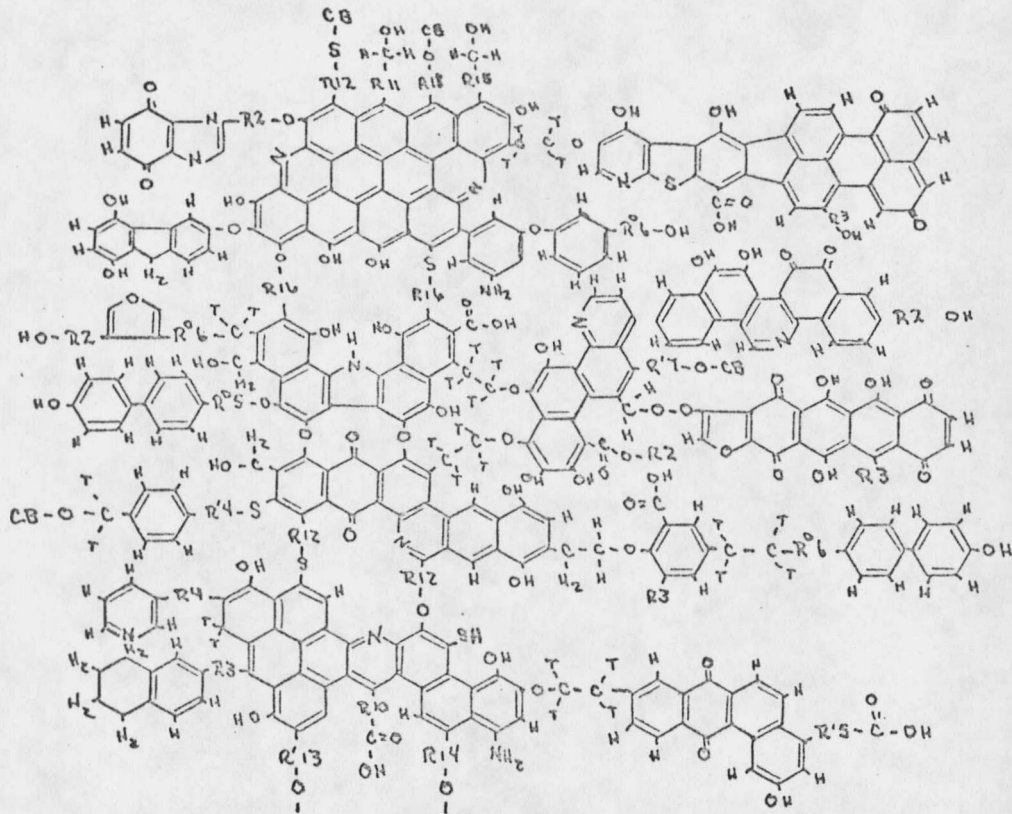
The United States' major source of energy and chemical feedstocks has been petroleum and most of the users are geared to the utilization of this form of energy. Thus, the ideal solution to the petroleum shortage would be to find a substitute source for liquid fuels. The

search for new liquid fuels invariably leads to coal because of the immense coal reserves which the U.S. has available. The United States has 16.5% of the world total recoverable coal resources (mapped and explored) [4]. Coal makes up 94.5% of the U.S. fuel reserves [6].

B. Coal Structure and Hydrogenation and Cracking to Produce Useful Products

Coal is a carbonaceous rock derived from wood and other plant tissues which flourished millions of years ago. Apparently the plants partially decayed and then were covered, preserved, and ultimately compacted by the other sediments that were deposited on them. Coals are actually intricate mixtures of complex compounds of carbon. Coals differ from one another in composition and properties, and even the various constituents of any one coal may be quite unlike [4].

In characterization work done on high volatile bituminous coals it appears that long chain, simple aliphatic and alicyclic hydrocarbon groups predominate in these coals. Multiple polynuclear ring structures are apparently absent. Although coals were once thought to have a chicken-wire structure of 50 to 60 of these ring structures tied together, it now seems more logical to assume that only five or six combine for each aggregate. A model of a high volatile bituminous coal is presented in Figure 1 [7].



CROSS BONDING TO MORE
HETEROCYCLIC GROUPS

$R^{\circ}N$ - Alicyclic rings of N carbons

RN - Alkyl side chain of N carbons

$R'N$ - Unsaturated alkyl side chain of N carbon

CB - Cross-bonding by O or S to new heterocyclic groups with side chains

T - Tetrahedral 3-dimensional C-C bonds, C-O bonds, and C-S bonds

Figure 1. Typical Cross-bonded Structure for High Volatile Coals

In the coal liquefaction process, it is generally believed that the hydrogenation process is accompanied by the decomposition or cracking of the high molecular weight compounds to smaller fragments [7,8]. If coal is heated in a normal carbonization process, thermal cracking and polymerization-condensation reactions occur, the products being paraffins, olefins, aromatics, tar, coke, char, and polycondensed pitch. If, however, when the coal is heated it is done so in the presence of a catalyst and hydrogen pressure, the amount of polymerization is controlled and more usable products are obtained from the same amount of coal. The typical products obtained in this case are alicyclic alkylated aromatic polycyclic products and gases as well as some coke. The liquid products can be further hydrotreated and hydrocracked to produce isoparaffins, aromatics, paraffins, naphthenes, and hydrocarbons [7].

Investigations have shown that an increase in the carbon content and decrease in the hydrogen content of the coal, i.e., with increase in the C:H ratio from 16.0 to 22.4, the conversion of the organic matter and the yield of the liquid products decrease; almost no liquid products are obtained from the hydrogenation of anthracitic coal. Thus, a connection exists between the organic coal matter and the yield of the liquid product; the C:H ratio should ideally not exceed 16. [3,9].

C. Products of Coal Liquefaction

The liquid products obtained from coal liquefaction are generally classified as one of three types. The classifications made are based on the solubility of a portion of the product in an organic solvent. These classifications are:

- (1) Oils - the portion of the liquid product which is soluble in hexane.
- (2) Asphaltenes - the portion of the liquid product which is soluble in benzene or toluene, but insoluble in hexane.
- (3) Aspholtols or pre-asphaltenes - the portion of the liquid product which is soluble in pyridine but insoluble in hexane or benzene and toluene.

The oils are the desired product since these may be directly worked with in typical refinery operations. They are the most highly hydrogenated portion of the overall liquid product.

Asphaltenes are generally of a polynuclear aromatic structure. The production of asphaltenes is not desirable since any further hydrogenation of asphaltenes is a very difficult step [10]. Asphaltenes hydrogenate to oils only slowly. Investigations have shown that asphaltenes are hydrogen-bonded acid-base complexes having components that can be separated. A separated moiety has only an acid or base

character, i.e., amphoteric species are not present. Thus, asphaltenes have a salt-like character [11].

Little seems to be presently known about the character of asphaltols. They appear to have the characteristic of highly functional polyphenols with greater than 10% heteroatoms. They have a higher oxygen content and increased basicity of nitrogen over that of the asphaltenes. Asphaltols are rich in chemical functionalities and may readily cross-link or polymerize. They contain hydrogen at a higher H/C value than 0.5 [11].

Slower reactions convert asphaltenes and asphaltols to oil product which generally occurs with a diminution of the heteroatom content of the material. Regressive reactions compete with the progressive reactions. For example, an asphaltene might regress to become an asphaltol or semi-coke [11].

Mobile Research and Development Corporation has defined a process for better characterizing the reaction products from coal liquefaction. Reaction products are fractionated using sequential elution with specific solvents through silica gel. The solvents used are:

1. Hexanes (mixed isomers)
2. Hexanes with 15% benzene
3. Chloroform
4. Chloroform with 10% diethyl ether

5. Diethyl ether with 3% ethanol
6. Methanol (absolute)
7. Chloroform with 3% ethanol
8. Tetrahydrofuran
9. Pyridine

The products are separated into fractions which have been identified as follows:

1. Saturates
2. Aromatics
3. Polar aromatics; non-basic nitrogen-, oxygen-, and sulfur-heterocyclics
4. Simple phenols
5. Basic nitrogen heterocyclics
6. Highly functional molecules, with greater than 10% heteroatoms
7. Polyphenols
8. Increasing oxygen content and increasing basicity of nitrogen
9. Like 8, only more so
10. Non-eluted, unknown materials

Broadly, with some overlap, fractions one and two may be identified as the oil fraction; fractions three, four, and five may be identified

with the asphaltene fraction; and the remaining fractions are the asphaltols [11].

D. Recent Coal Liquefaction Processes

Pilot plant studies can be divided into two classes--coal hydrogenation processes and coal pyrolysis processes, in which the coal is decomposed into liquids by heat. One of each will be discussed here.

The Synthoil process, which has been developed by the U.S. Bureau of Mines, utilizes crushed coal which is then slurried with a coal derived oil. The slurry and turbulently flowing hydrogen are fed to a fixed bed catalytic reactor, in which the coal is liquefied and desulfurized. The yield is about three barrels of low sulfur fuel oil per ton of coal. Other coal hydrogenation processes include the H-coal process developed by Hydrocarbon Research, Inc. [12,16,30].

In the COED process developed by the FMC Corporation, crushed coal is heated to successively higher temperatures in a series of fluidized bed reactors. After further processing, the main products are syncrude, fuel gas, and a residual char. The syncrude yield is about one barrel per ton of coal. Another coal pyrolysis process is the Oil Shale Corporation's Toscoal Process [5,12,16,30].

E. Rapid Coal Liquefaction Through Use
of Tubular Reactors

Research studying the rapid hydrogenation of coal in tubular reactors is currently being conducted at two other known locations. Cities Service Research and Development Company has developed a process of this type. In their operation, dry pulverized coal is fed in batches to a hopper, which is then pressurized to reactor pressure with hydrogen. A star-wheel feeder then feeds the coal through a standpipe into the reactor, where it mixes with preheated hydrogen. The coal falls freely through the reactor to a char pot, devolatilizing on the way. A cold quenching medium quickly cools the remaining char. The product gas mixture passes through sequential heat exchangers where the liquid products are withdrawn from the hydrogen stream. Residence time in the reactor varies from 100 to 300 milliseconds. Heat up rate for the coal can be varied from 50,000 to 150,000°F per second. With this continuous bench scale apparatus, Cities Service has processed coal at rates up to 2 lbs per hour with 50 to 80% conversion [13].

Research using coiled tubular reactors is also being carried out at the University of Utah. Their process has been through several bench scale phases which have been directed toward a short contact time and high hydrogen to coal rates under moderate reaction conditions. They also use a hopper with star-wheel feeder to feed the

coal to the reactor. From the hopper, the coal passes through a 20 foot long preheater to bring it to the desired reaction temperature. The coal is then held at the reaction temperature for the desired time (1 to 6 seconds) by the choice of tube length. The reactor configuration is a coiled tube which is operated at temperatures of 500 to 550°C and hydrogen pressures of 1600 to 2000 psi. They have obtained conversions as high as 58.5% for ZnBr_2 catalytic coal [14,15].

Recent research has shown that in the rapid heating and hydrogenation process utilized in the coiled tube method of coal liquefaction, the formation of tars and char is partially eliminated. The liquefaction of coal appears to take place in a very short time period. If the coal and liquefaction products are held at an elevated temperature for a longer degree of time, no additional coal conversion is obtained, rather the amount of useful products decreases through polymerization reactions and forms less useful products such as char (see Figure 2) [11]. Cities Service reports that the conversion of coal in their system has been accomplished without the production of high-boiling tars although some char is produced [13]. Work done at Pennsylvania State University indicates that coals generate the greatest amount of volatile matter yield if heated to reaction temperature at very high rates to prevent crosslinking reactions that may reduce yield [1].

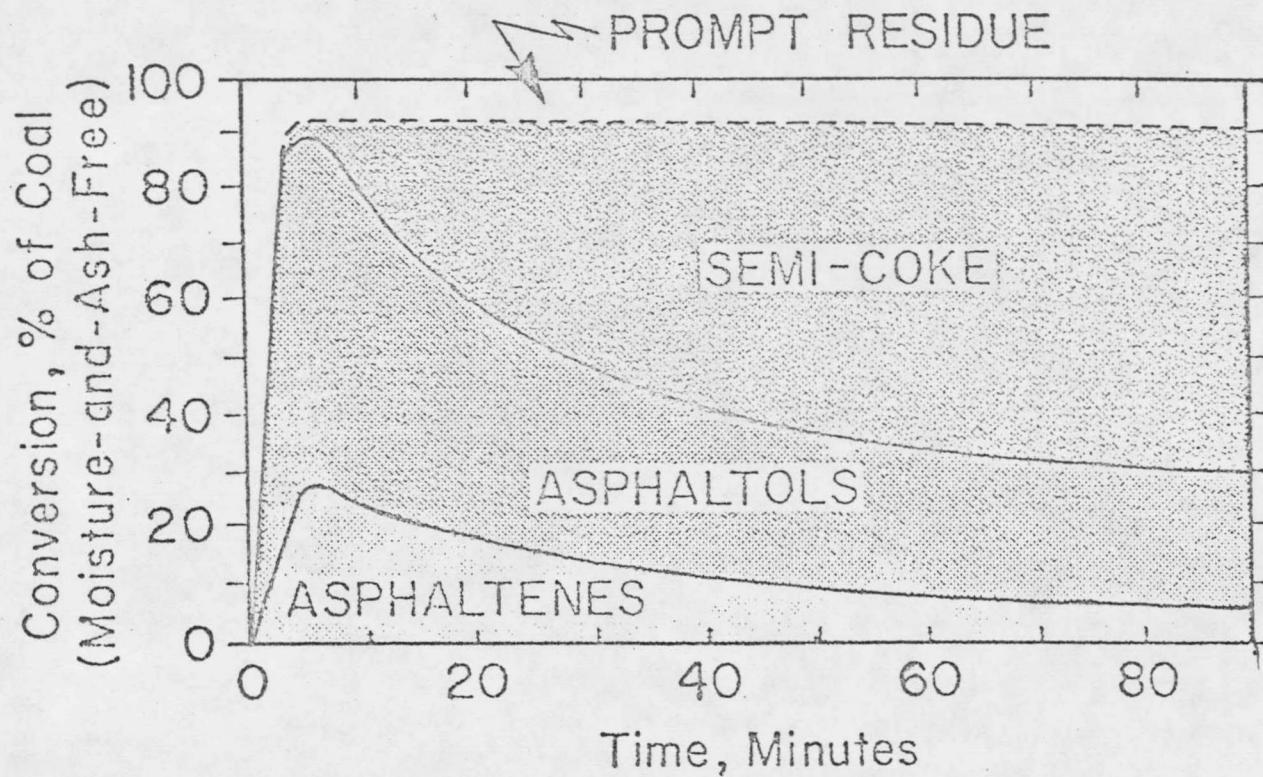


Figure 2. Conversion of Coal vs. Time of Reaction

The rapid formation of desirable products is, then, one of the advantages that liquefying coal in short residence time tubular reactors has over some of the other coal liquefaction processes that have been developed. The simplicity of equipment may also be an advantage since there is no coal solvent, etc., involved as there is in some of the other processes [16,30].

RESEARCH OBJECTIVES

The objectives of this research were threefold:

1. To design and construct a continuous and hydrogenation system utilizing the rapid liquefaction, tubular reactor principle.
2. To eliminate and solve operational problems inherent in the operation of the equipment in order that meaningful and accurate data could be obtained thus making the research efforts beneficial in helping to expand the current coal technology base.
3. To preliminarily test what effect the variables which exist in the equipment have upon coal conversion, namely temperature, pressure, hydrogen flow rate, coal feed rate, reactor length, and catalyst presence in the coal, both by impregnation on the coal and mixing with the coal. This reactor system will be further used in more in-depth catalyst screening studies as well as for better characterization of how the other variables also affect coal liquefaction.

EQUIPMENT DESIGN AND CONSTRUCTION

A. Overall Process

The abstract of proposed research stipulated the type of equipment which would be needed for this research, i.e., a continuous reactor system which utilizes a high pressure star feeder for continuous powdered coal feed [17]. From this, an overall flow diagram was developed (see Figure 3). Since it was planned to use gaseous HCl in the system, all parts were necessarily made of inconel where possible.

B. Coal Star Feeder

The next step in the design of the equipment was to design or specify each individual piece. The coal star feeder (see Figure 4) was supplied by William D. Peterson and Associates of Murray, Utah. The feeder and hopper unit was constructed of inconel for corrosion resistance. A rotating star shaft of one cubic centimeter volume per shaft revolution was specified. The feeder was driven by an electrically powered motor with variable speed output allowing the speed of the feeder shaft to vary from 0.20 revolution per minute to 3.3 revolutions per minute.

C. Reactor and Heater Assembly

The reactor assembly (see Figure 5) was designed and built at MSU. The heating section for the reactor consists of five nichrome wire heaters (22 gauge) insulated with ceramic beads and coiled on the

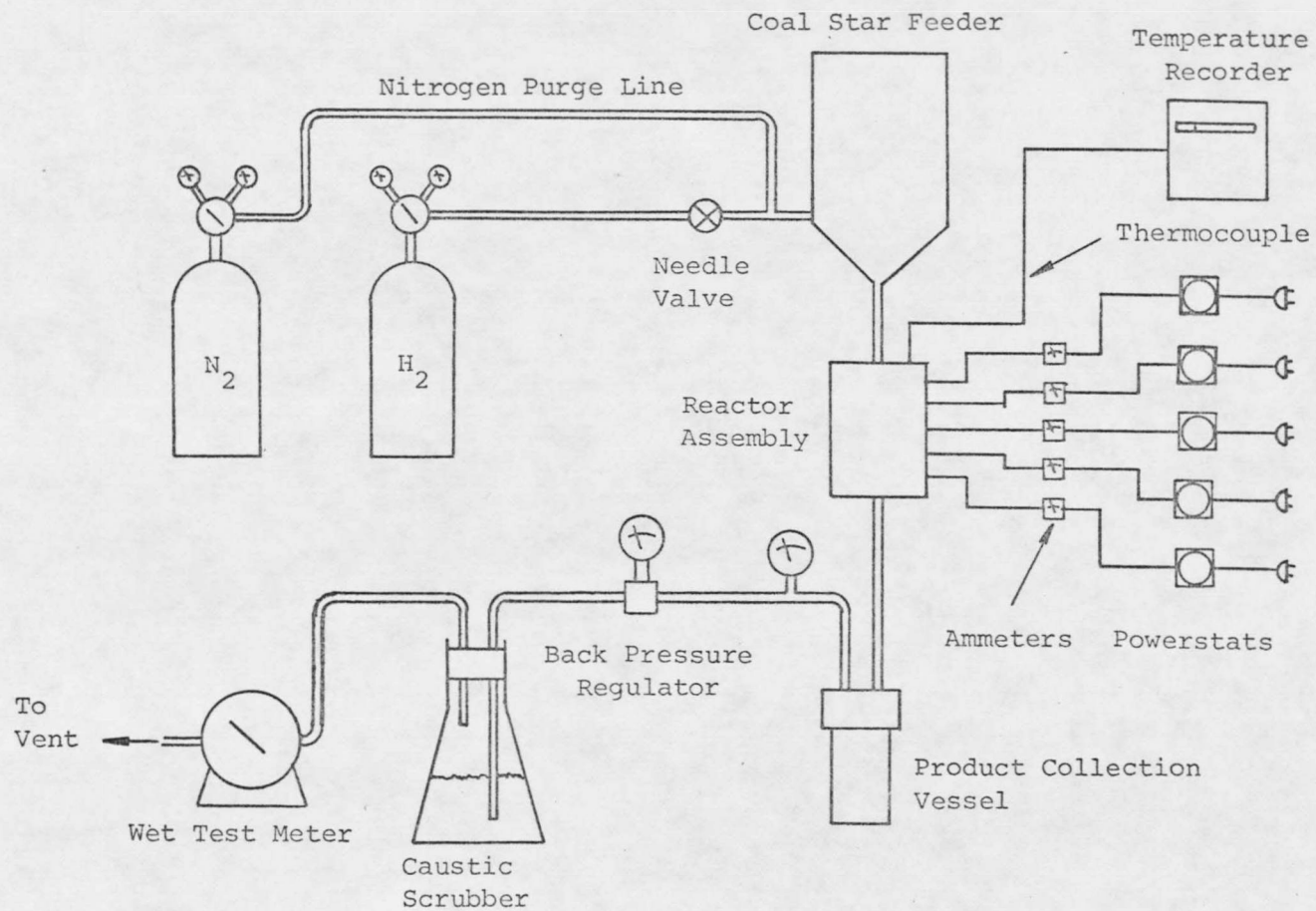


Figure 3. Equipment Flow Diagram

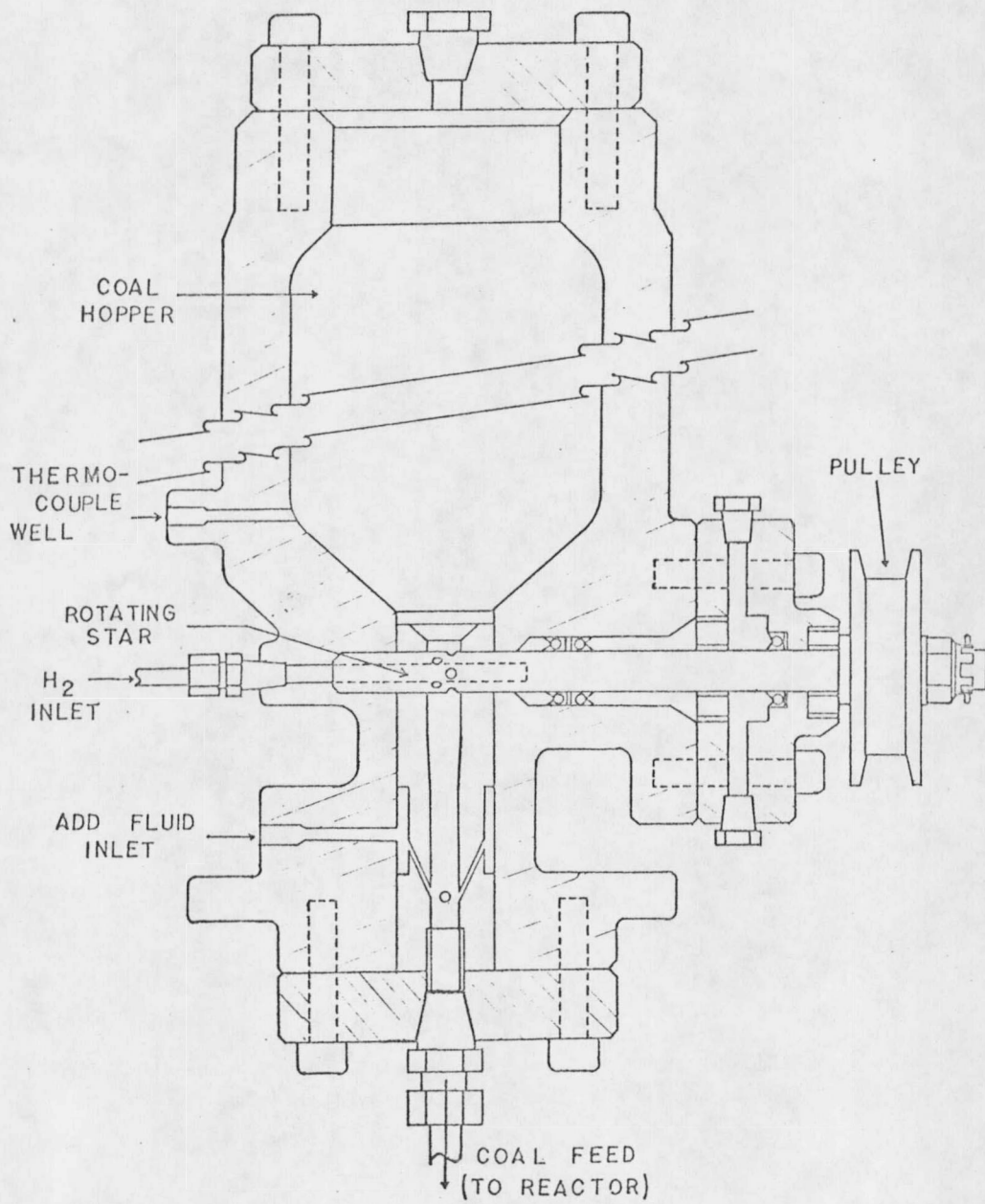
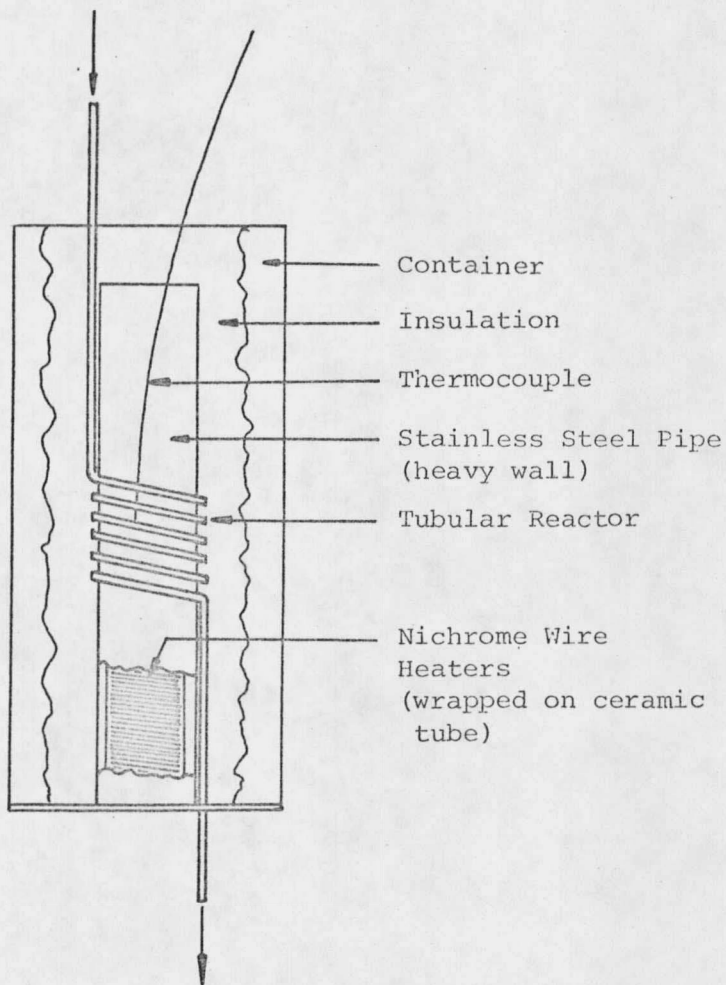


Figure 4. Coal Star Feeder Detail

From Star Feeder



To Product Collection
Vessel

Figure 5. Reactor and Heater Detail

outside of a 2-7/16" O.D. ceramic tube which provides a support for the heaters. Power to the heaters (or reactor temperature) is controlled by powerstats and the current flow is measured by inline ammeters. The length of the individual heaters was determined by taking into account the maximum amperage load rating of the powerstats which were to be used as controlling units, the voltage of the electrical source (110 volt wall plugs), and the resistance of the nichrome wire. This was done through use of the formula:

$$V = IRL,$$

where V = voltage

I = current

R = resistance of wire per unit length

L = length of wire

Through rearranging and solving for L, substituting the maximum amperage rating of the powerstats for I, the line voltage for V, and the resistance R of the wire, the shortest allowable heater length could be found for which the powerstat fuses would not burn out with the powerstats set at maximum amperage output. The minimum length of wire is important (in this case 14 feet) since through use of the minimum allowable length the maximum temperature for that particular gauge of nichrome wire can be obtained. Five heaters were used since the length of the ceramic core was just long enough to provide the

space necessary to support the number of wire wraps for five heaters. The heater capacity as designed is very adequate to provide the necessary heat for the reactor; heat-up time to 500°C from ambient temperature is only a half hour with the powerstats set at mid-range.

The heater assembly fits inside a heavy wall (1/2 inch wall thickness) stainless steel pipe 24 inches long with an O.D. of 3-1/4 inches. The reactor is then coiled to fit around the outside of the heavy pipe. The heavy walled pipe was used to provide an approximate isothermal heat source for the reactor. The reactor is fully insulated externally.

The reactors used in this equipment were constructed of 1/4 inch stainless steel tubing having a wall thickness of 0.065 inches. Reactors of various lengths were constructed, namely 6, 12, and 18 feet.

D. Temperature Measurement, Product Collection

The reactor temperature was measured through the use of a chromel-alumel thermocouple attached to a Honeywell temperature recorder. The thermocouple was placed between one of the reactor coils and the outside wall of the heavywall pipe (see Figure 5 for more detail).

The product collection vessel used in this research was a batch-run autoclave with cover modified to accept standard Swagelock fittings. An autoclave was used since a container was needed that was

known to be pressure tested beyond the reaction pressures which were to be used.

E. System Pressure and Hydrogen Flow Measurement

Pressure on the system was maintained through the use of a Grove Mighty-Mite back pressure regulator. This regulator was modified in that the parts which were to be wetted by the reaction gases were re-machined from inconel. This was again for reason of corrosion resistance.

The hydrogen gas supply to the system was compressed hydrogen from gas cylinders with pressure regulator delivery. Control of the gas flowrate was accomplished with a needle valve. The gas flowrate was initially measured with a Brooks hydrogen mass flowmeter placed in the hydrogen supply line between the hydrogen cylinder and the coal feeder. Use of the mass flowmeter was discontinued when it was found that hydrogen flowrates beyond the meter's capability were needed to prevent reactor plugging. Measurement of the hydrogen flowrate was then accomplished through the use of a wet test meter (see Figure 3 for more detail).

OPERATIONAL PROBLEMS

All of the operational problems in the equipment as constructed were encountered in the coal star feeder. The problems were of two types--gas leakage and difficulty in continuously, accurately, and reproducibly feeding the pulverized coal to the reactor system.

The gas leakage problem occurred between the coal hopper lid and the coal hopper rim (see Figure 4). The method of attempted seal was through the use of an "O"-ring and machined "O"-ring groove in the hopper rim. When cap bolts securing the hopper lid to body were tightened, sufficient contact of the "O"-ring with its mating surfaces were supposed to stop gas flow between the mating surfaces. The "O"-ring did not perform as expected and sealing was obtained only after the "O"-ring was coated with grease, allowing it to move more freely in its groove.

The other problem encountered was that of actually feeding the coal to the reactor. The star feeder would feed the pulverized coal for only a short time after it was put into operation. The coal feed-rate would decrease rapidly until coal feed stopped completely. Several possible solutions to this problem were examined.

The first possible solution to the feed problem which was examined was that of drying the coal. Dry coal seemed to exhibit better flow characteristics than did the moist coal as pulverized. Testing

indicated that while feeding seemed to improve with the use of dried coal, the feeding obtained was still very sporadic.

Another attempt to solve the problem examined the exit tube from the feeder prior to the reactor tube entrance. It was thought that perhaps bridging of the coal was occurring at this point since the coal had to pass through a reduction in tube size from the 1/2 inch diameter of the feeder exit tube to the 1/4 inch diameter of the reactor tube. A vibrator was attached to the exit tube in an attempt to disperse any bridging that might be occurring at this point in the system. This did not solve the feeding problem.

Based on the above attempt to improve the feeding characteristics of the star feeder, it was concluded that bridging of the coal must be occurring over the rotating star shaft itself. With this in mind, the next attempts at improving the coal feed were aimed at physically moving the coal within the hopper in order to collapse any possible bridge that could be forming over the rotating shaft.

In the first attempt to move the coal over the shaft, a funnel was hung directly over the rotating shaft on a rod which was inserted through the thermocouple well into the hopper body (see Figure 4). A vibrator was attached to the end of the rod which protruded outside the hopper body with the idea that the vibrations would carry through the hopper wall and vibrate the funnel. When the funnel was filled with coal, however, it proved to be too massive and all vibration was

damped out. As a result, the attempt to vibrate the coal over the rotating shaft failed.

In the next effort to improve the coal feed, a vibrating motor was attached to the top of the hopper with the idea that vibrating the hopper would, in turn, vibrate the coal within the hopper breaking up any bridging that might be occurring. This effort failed mainly because the hopper and star feeder proved to be too massive and beyond the capability of the vibrating motor.

In the next endeavor undertaken to improve the feed, a mechanically driven stirrer was placed through the opening in the hopper lid (see Figure 6). The shaft of the stirrer was sealed to gas leakage by using a Teflon-packed stuffing box which provided adequate sealing to the maximum 1000 psig pressure tested. The stirrer was driven by an electric motor with constant speed gear reduction giving the stirrer a speed of about two revolutions per minute. The stirrer was positioned so that its end was located just above the rotating star shaft. Wings were welded to the stirrer to aid in moving the coal. The use of the mechanically driven stirrer greatly improved the feeding characteristics of the star feeder. Feedrates of 0.68 to 2.55 gms coal fed per hour were obtained without varying the shaft speed of the rotating star. Thus, it was also seen that while better feeding characteristics were obtained, the feedrates observed were not at all reproducible.

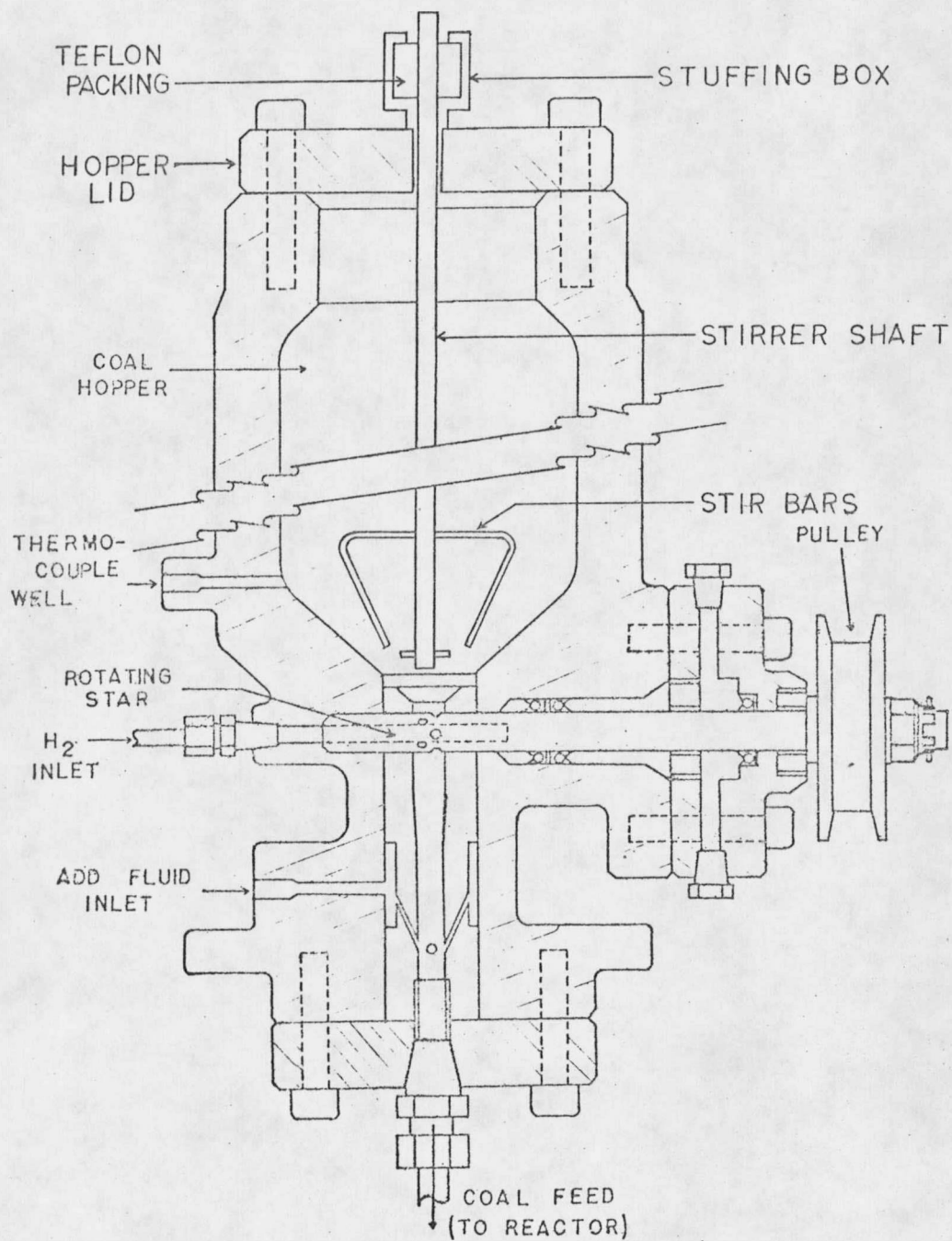


Figure 6. Coal Star Feeder with Stirrer Installed

In an attempt to improve the reproducibility of the coal feedrate, the 1 cm³ per revolution star shaft was replaced by a shaft which had a feed volume of 3 cm³ per revolution (see Figure 7). With this replacement the reproducibility was improved to the point in which the maximum variance observed between runs was less than 4% in the tests made. With the new star shaft, the coal feedrate could be varied between 1.68 to 7.96 gms coal fed per hour by changing the shaft speed of the rotating star. This was still a much lower feedrate than the theoretical feedrate calculated on the basis of total star volume per star shaft revolution (see Table I).

Table I also shows that the actual coal feedrate obtained is inversely proportional to the shaft speed of the rotating star. It is hypothesized that the reason for this occurrence is that at slower rotating star shaft speeds, the star cavities are visible to the mechanically driven stirrer for a longer period of time. This enables the stirrer to more completely fill the star cavities.

Table I. Rotating Star Shaft Speed, Theoretical Coal Feedrates, and Actual Coal Feedrates

Feeder Speed Setting	Shaft Speed (rpm)	Theoretical Coal Feedrate (gms/hr)	Actual Coal Feedrate Obtained (gms/hr)
5	1.35	112.50	7.96
10	2.12	209.89	2.31
18	3.38	334.65	1.68

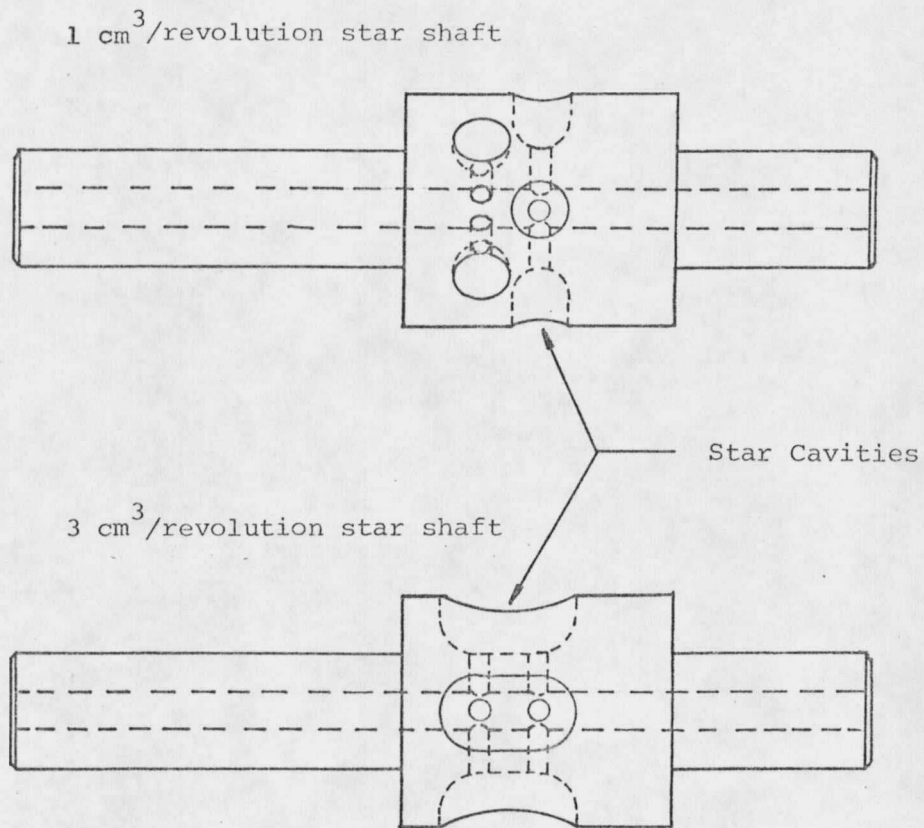


Figure 7. Views of 1 cm³ and 3 cm³ Star Shafts

MATERIALS, EQUIPMENT, AND PROCEDURES

A. Preparation and Analysis of the Coal

The coal used in this research was a sub-bituminous coal mined from the Rosebud bed near Colstrip, Montana. The coal was supplied by Western Energy Company in 1975 and has been stored in plastic lined metal drums to prevent any compositional changes. The proximate and ultimate analysis of the coal is given in Table II.

The coal was taken from the metal drums, charged to a ball mill and pulverized. After the ball mill had run for twenty-four hours the coal was removed from the ball mill and was screened to -50 mesh. The screened coal was then placed in plastic sacks for storage until needed. Prior to the charging of coal to the feeder, it was dried a minimum of forty-eight hours. The attempt was made to treat all coal samples the same so that any possible alterations of coal composition which may have occurred would also be the same for each coal sample.

Conversions of the coal were determined on a moisture and ash-free (MAF) basis. This required an analysis of the moisture and ash content of the coal. The moisture analysis was performed using the apparatus shown in Figure 8. Toluene and a weighed amount of coal along with boiling chips were charged to the boiling flask. The rising toluene and water vapor were condensed, falling to a graduated receiving arm. The water, having a greater density than the toluene, settled to the bottom of the receiving arm. From the volume of water

Table II. Analysis of the Colstrip Sub-bituminous Coal [18].

Proximate Analysis

Moisture (as received)	23.9%
Volatile Matter (MF)*	40.6
Fixed Carbon (MF)	49.4
Ash (MF)	10.0

Ultimate Analysis (MF)

Carbon	66.1%
Hydrogen	4.5
Nitrogen	0.9
Sulfur	0.5
Oxygen	18.0
Ash	10.0

Analysis of Major Ash Components

SiO ₂	36.4%
Al ₂ O ₃	17.6
Fe ₂ O ₃	4.6
TiO ₂	0.4
P ₂ O ₅	0.8
CaO	22.7
MgO	9.4
Na ₂ O	0.3
K ₂ O	0.5
SO ₃	14.9

* MF = moisture-free basis

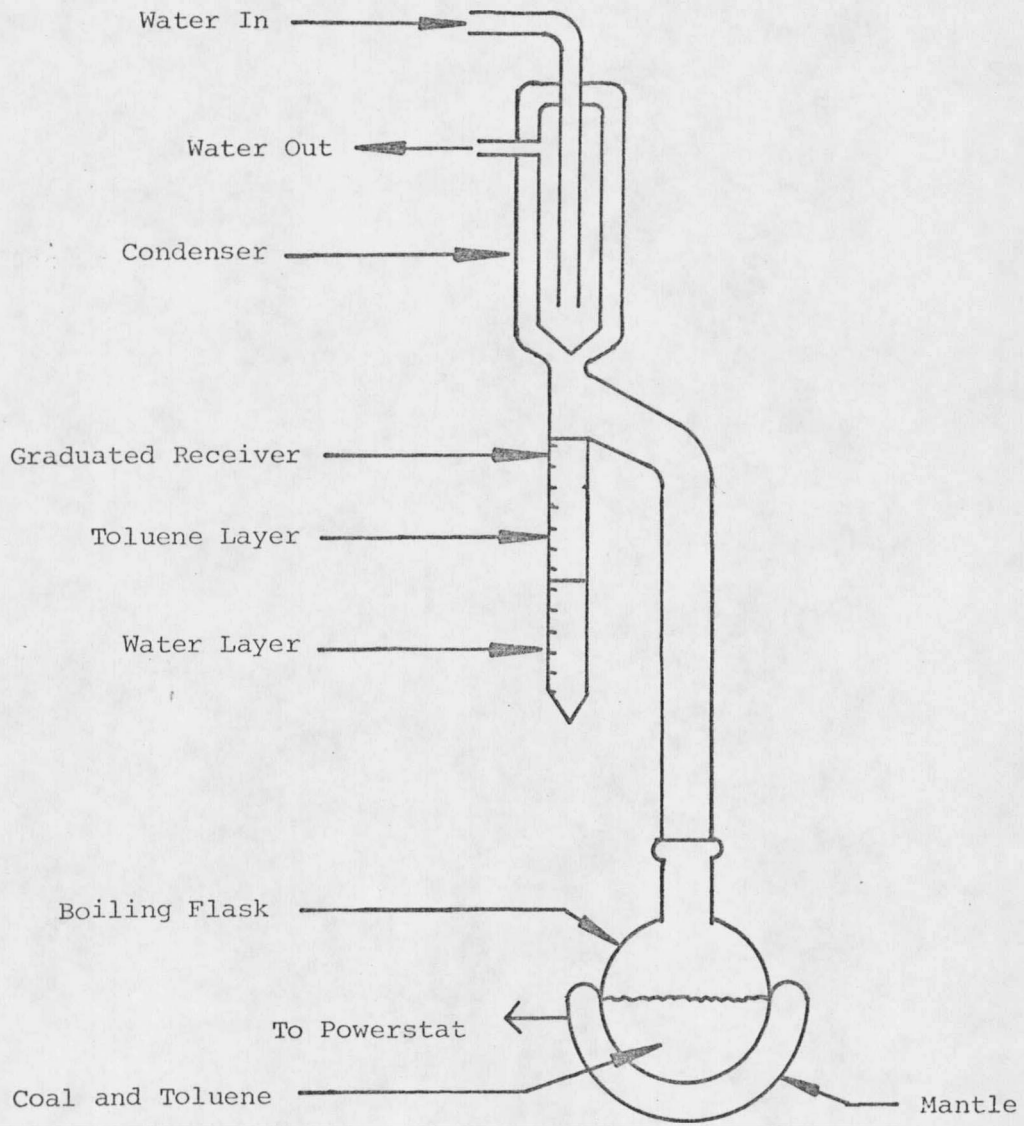


Figure 8. Apparatus Used to Determine Water Content of the Coal

present in the receiving arm and the weight of the initial coal charge, the water content of the coal was calculated. This analysis was allowed to run for twenty-four hours.

The ash content of the coal was determined by heating a weighed amount of coal in a covered porcelain crucible. This drove off any volatile components in the coal sample. After the volatile components were driven off, the lid was removed from the crucible and the fixed carbon was oxidized. The residue remaining was weighed and, knowing the weight of the initial coal charged, the ash content of the coal was calculated. Ash analyses were performed only at the beginning of this research; it was assumed that in ball milling the coal, thorough mixing would occur and any one sample of the coal would be representative of the total screened coal.

B. Preparation of Catalytic Coal

Three technical grade catalysts were examined in this study: nickel chloride, stannous chloride, and stannic chloride. The catalysts were both impregnated on the coal as well as physically mixed with the coal. To compare the activities of the catalysts tested, solutions containing equivalent weights of the respective metals were prepared. The coal to be catalytically treated was dried at 100°C for forty-eight hours prior to treating.

The coal which was to be treated by impregnation of the catalyst was added to the catalyst-water solution, the coal having been previously weighed. The mixture was stirred intermittently for twenty-four hours. After the soaking process, the catalyst-water solution was filtered from the coal. The coal was then dried and re-weighed. The weight gained by the coal was used to determine the amount of catalyst impregnated on the coal.

The impregnated coal samples were prepared and the percent catalyst concentration for each respective catalyst was used to prepare the coal mixed with catalyst. This allowed preparation of impregnated coal and mixed coal with the same catalytic content for each catalyst tested. In this way, the effects of impregnated or mixed catalyst on coal conversion could be compared without needing to account for differences in catalyst contents. In preparation of the mixed coal a weighed amount of dried coal and predetermined amount of catalyst were placed together in a small ceramic ball mill. The mill was allowed to run for four hours at which time the coal was placed again in a dryer to remove any moisture that the coal mixture may have absorbed during the mixing process as well as to remove the water from the hydrated catalysts.

C. Procedure for Performing Test Runs

In performing a test run, a dried coal sample was charged to the star feeder hopper. The system was pressurized to the run pressure with nitrogen and a bleed flow of nitrogen was started in order to purge the reactor system of any air that may be present. The system was purged for safety reasons as it was undesirable to have any oxygen present in the system when the flow of hydrogen to the system was started. This purging was done for the length of the reactor heat-up time. At the same time that the nitrogen purge was started, the reactor heat-up was also begun. Ambient conditions were recorded at the beginning of each run.

When the reactor had reached the desired run temperature, the hydrogen flow was started and its flowrate established. At this time the coal feeder and stirrer were started, beginning the actual run.

During the run, the reactor temperature was monitored and the current to the reactor heaters was adjusted as necessary. The hydrogen flowrate was also monitored and adjusted since its flowrate did not remain constant at the setpoint made prior to beginning the run. The wet test meter measured all reaction gases as well as the hydrogen which was not used in reaction. It was thus assumed in this research that the amount of hydrogen used and the amount of reaction gases produced were approximately equal and that any error introduced by this assumption was insignificant when compared to the total flowrate

of the unreacted hydrogen. No qualitative or quantitative analysis attempts were made in this research to characterize the reaction off-gases.

The run was allowed to proceed for approximately one hour. At run completion, the system pressure was bled off and the product collection vessel was removed from the system. The collection vessel was opened and its contents were removed and tested for liquid conversion.

D. Determination of Conversion

The conversion in the research was determined on the basis of three solvent extractions. The product was first extracted with cyclohexane yielding product oil content; the next extraction of the product was made with toluene, yielding the asphaltene content; and the last extraction was done with pyridine which determined the asphaltol content of the product [18]. The total conversion of the coal was determined by summing the conversions from each of these extractions. The extractions were made through the use of a Soxhlet apparatus (see Figure 9).

The product removed from the product collection vessel following each experimental run was weighed and placed in a pre-dried double thickness cellulose extraction thimble. The thimble and product were then placed in a Soxhlet extraction apparatus (see Figure 9). The solvent vapor from the boiling flask would rise through the side arm

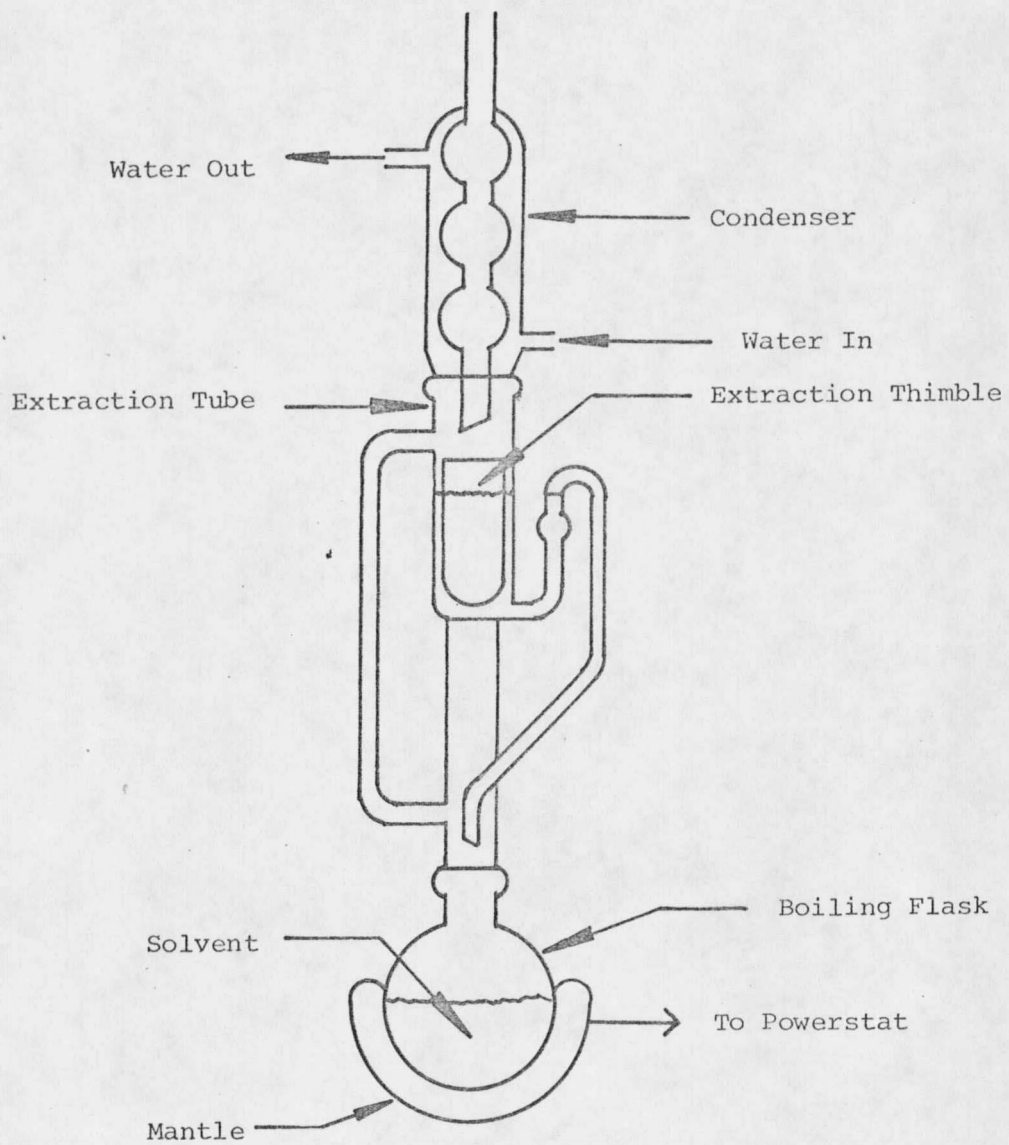


Figure 9. Soxhlet Extraction Apparatus Used to Determine Coal Conversion

and up into the condenser. The solvent condensed and dripped into the extraction thimble. When the solvent height reached the upper level of the siphon arm, the solvent was automatically siphoned through the extraction thimble and back into the boiling flask, carrying with it any soluble portion of the product that it may have picked up.

Each extraction was allowed to progress until the liquid siphoning through the thimble was clear. The length of time required for complete extraction varied with the reflux rate and the solvent being used.

After each extraction was complete, the thimble and its residual contents were removed from the apparatus and allowed to air dry after which they were placed in a drying oven at 100°C for twenty-four hours. All product samples were treated in this manner, so if any product degradation or compositional change occurred, it should have been uniform. After the thimble and residuals had dried, they were weighed. This procedure was performed for each of the solvents and for each product. This analysis was also performed for unreacted coal to determine the amount of the soluble components present in the coal before reaction.

The difference in thimble weights before and after the extraction represented the amount of the product converted to that respective product--oil, asphaltene, or asphaltols. By knowing the water, ash, and catalyst (for catalytic coals) content, the moisture, ash, and

catalyst free (MACF) content of the charge coal could be calculated (for non-catalytic coal MAF). By taking into account the lost weight by extraction and the MAF or MACF content of the coal as well as the respective fraction of the unreacted coal charged which was soluble in that particular solvent, the conversion of the charged coal to oils, asphaltenes, or asphaltols could be calculated by using the following equation:

$$C = (\ell/\text{MAF}) \times 100\% - U \quad \text{non-catalytic coal}$$

$$C = (\ell/\text{MACF}) \times 100\% - U \quad \text{catalytic coal}$$

C = % conversion of coal to the respective product for that solvent,

MAF = weight of moisture and ash free material present in the total liquid and solid product collected,

MACF = weight of moisture, ash, and catalyst free material present in the total liquid and solid product collected,

ℓ = weight loss during respective extraction,

U = respective percentage of solubles present in unreacted coal for that particular solvent.

Conversion calculated on this basis identifies how much the coal has been upgraded during the reaction process. The total conversion is determined by summing up the individual conversions obtained for each solvent on the particular product sample.

It should be noted that no attempt was made in this research to quantify the amounts of light gases which were produced. Thus, the conversions obtained and reported are based on conversion of the coal to liquid product only, the conversion of the coal to gaseous products was not studied.

RESULTS AND DISCUSSION

A. Coal Analysis

Ash analyses were performed on the coal used in this research. The analyses were performed only initially since it was assumed that, in the pulverizing process, the ground coal would be thoroughly mixed and any small sample should be representative of the total. The results from the ash analyses performed agreed closely with the ash analysis for this coal reported in the literature [20].

The coal used in this research was also tested for its water content before drying. The coal was found to contain 20.3% water. This is somewhat less than the moisture content of this coal which is reported in the literature--23.9% [20]. This difference may be due to coal water loss while in storage or to differences in water analysis methods between those used in this research and those used to obtain the values reported in the literature.

Since it was found that the coal would need to be dried before using it in the experimental equipment, studies were undertaken to determine the equilibrium drying time required for the coal. As a result of this research, the coal drying curve in Figure 10 was obtained. The results showed that the required equilibrium drying time for the coal was reached after about 48 hours at 104°C. A toluene water analysis was performed on the dried coal and it was found to contain about 1% residual water after the equilibrium drying time was reached.

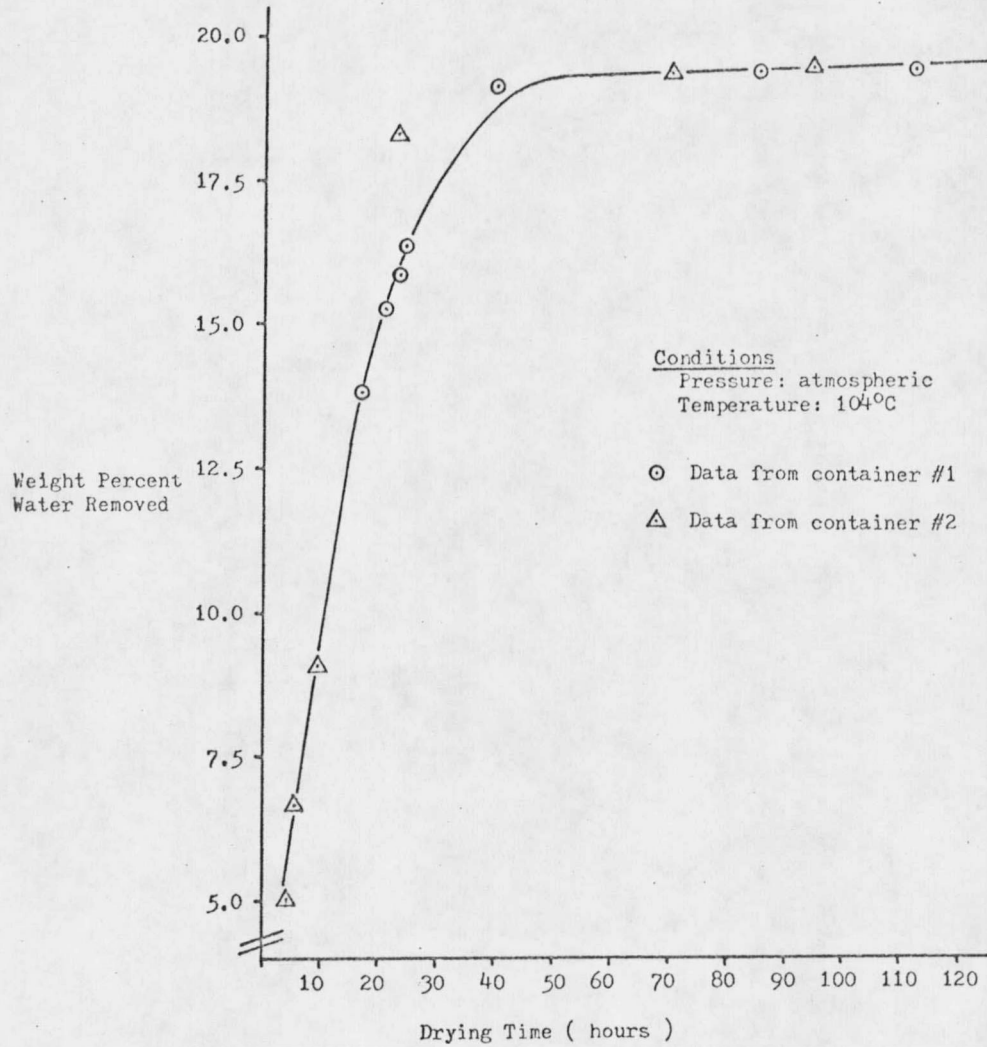


Figure 10. Coal Drying Curve

Storage, pulverizing, and drying the coal used may have significantly affected its reactivity. Research performed by the U.S. Bureau of Mines has indicated that aging of lignite coal had a detrimental effect on conversion. Exposure to the air for four weeks caused a drop in conversion from 90% to 77% when conversion of coal was accomplished through the CO-steam process. Drying the coal at 105°C for 24 hours dropped the conversion to 54%. It was also observed that coal conversion was affected by the water content of the coal [21].

The literature also reports that charcoal will chemisorb substantial quantities of oxygen at room temperature in seconds. The mild oxidation with air or O₂ adversely reduced its reactivity for methane formation [1].

Freshly mined coal is chemically very active. Certain constituents have a marked affinity for oxygen, with which they enter into combination at ordinary temperatures. A very important factor is the coal particle size or the sum total area of the superficial areas of the particles and accessibility of oxygen to the mass [2].

Thus, it is certain that the reactivity of the coal used in this research was decreased both in the pulverizing as well as the drying process, since both of these processes allowed the air to contact the coal for significant periods of time. It is assumed in this research that, since the charge coal samples were all treated the same, the aging process would also uniformly affect the results.

Coal conversion was determined using three solvent extractions. The solvents used were cyclohexane, yielding product oil content, toluene, yielding asphaltene content of the product, and pyridine, determining the asphaltol content of the product. These solvents were chosen since the current trend of conversion reporting is based on these solvents [29]. Research has also shown that toluene may be substituted for benzene in determining the asphaltene content without significant differences [18].

Plain unreacted coal was also tested to determine the presence of any solubles in order that their presence would not be misconstrued as conversion. The unreacted coal was found to contain 0.70% oils, 0.73% asphaltenes, and 0.50% asphaltols.

Research was performed to determine the coal particle size distribution of the feed coal. The results are given in Table III. A possible solution the coal feeding problem considered for examination was that of working only with coal particles of a certain size range. The size range of particles chosen would have been done so on the basis of the flow characteristics of that size range. It is reported, however, that the coal particle size has a definite effect on conversion. This was due to composition differences in particles of different sizes, the smaller particles contained more brittle materials and were more easily pulverized. It was found that the smaller particle size ranges were more difficult to hydrogenate than the larger particle

Table III. Coal Particle Size Distribution of Feed Coal

Coal Size (Tyler std. mesh)	Weight %
50 x 60	0.23
60 x 80	3.30
80 x 100	17.55
100 x 150	35.35
150 x 200	31.54
-200	<u>12.03</u>
	100.00%

size ranges because of the compositional difference [22]. Since this was the case, it was decided to try to use the total -50 mesh coal as it was taken from the ball mill rather than use any portion of it.

The bulk density of the coal as ground in this research was determined experimentally as 0.55 gm/cm^3 .

B. Preliminary Research

Preliminary research was performed to determine the operability of the equipment, as well as some of its capabilities. Some of the results of the preliminary research are presented in Table IV. This research was carried out with the 1 cm^3 per revolution rotating star and coal feedrates were not at all reproducible. Conversion was determined on a basis of benzene solubles which determined, together, the oil and asphaltene content of the product [10]. This preliminary

research demonstrated the viability of this process for conversion of coal to liquids.

Table IV. Selected Results of Preliminary Research

Run	Ave. Run Temperature (°C)	Run Pressure (psig)	Ave. H ₂ flowrate (std. ft ³ /hr)	Ave. Product collection rate (gm/hr)	Benzene Soluble Conversion (%)
B-2	507	1000	7.13	2.55	11.95
B-8	505	1000	7.74	1.38	14.43
B-5	501	500	8.07	0.55	0.99
B-7	507	500	8.16	0.69	2.83

The preliminary research also seemed to show that a new stainless steel reactor may act as a catalyst for the conversion of coal. The initial conversion was much higher than for the rest of these experimental runs. This fact was not examined any further in this research. In the remaining experimental runs performed, any new reactor was operated for a minimum of four hours before any data was taken in order to eliminate any catalysis which the reactor walls may have exhibited.

From this preliminary research, it was concluded that coal conversion was increased at 1000 psig over the conversion obtained at 500 psig. This is consistent with what is reported in the literature: the use of increased hydrogen pressure considerably intensifies the

process of liquefaction of coal [3,23]. On this basis, all additional experiments were made at a pressure of 1000 psig.

In the remaining experimental research conducted, all runs were made at the standard conditions given in Table V, the variation being the variable which was being tested, i.e., all of these standard conditions were held constant during each of the experimental runs except for the variable being tested. None of the averages of the controllable variables for a given run, temperature and hydrogen flowrate, varied more than 2% from the desired standard value. Close control was maintained on these two variables during a run, resulting in the small deviation.

Table V. Standard Run Conditions

Temperature:	500°C
Pressure:	1000 psig
Hydrogen flowrate:	8 std ft ³ /hr
Coal feedrate:	2.31 gms/hr
Reactor length:	6 ft
Coal feed:	-50 mesh, dried, noncatalytic

C. The Effect of Temperature on Coal Conversion

As is shown in Figure 11, temperature had a very decided effect upon the coal conversion obtained. Temperatures tested were 300, 500, and 600°C. Conversion of the feed coal to liquids was increased with higher temperatures.

The increased conversion can be explained by a postulated mechanism for the hydrogenation of coal [24]. Coal is thermally split to form reactive fragments. It is probable that at the lower temperatures, there was insufficient thermal energy to split the coal into as many fragments. This would also reduce the number of active sites which would be present for hydrogenation.

These findings agree with those of other research reported in the literature. Research previously done at Montana State University shows that conversion increased with temperature through the maximum 600°C tested [10]. Research done by Wood and Wisler with an apparatus similar to that used in this research shows that temperatures of 650 to 700°C are required to achieve 60-65% conversion of the feed coal [14]. In a patent by Schroeder, again using a coiled tubular reactor, it is reported that if hydrogenation temperatures in the range of 600 to 1000°C are used and the heating period at temperatures above 300°C is less than five minutes, then conversion of coal to distillable liquids and gas can be "substantially completed in a very simple and economic manner" [25].

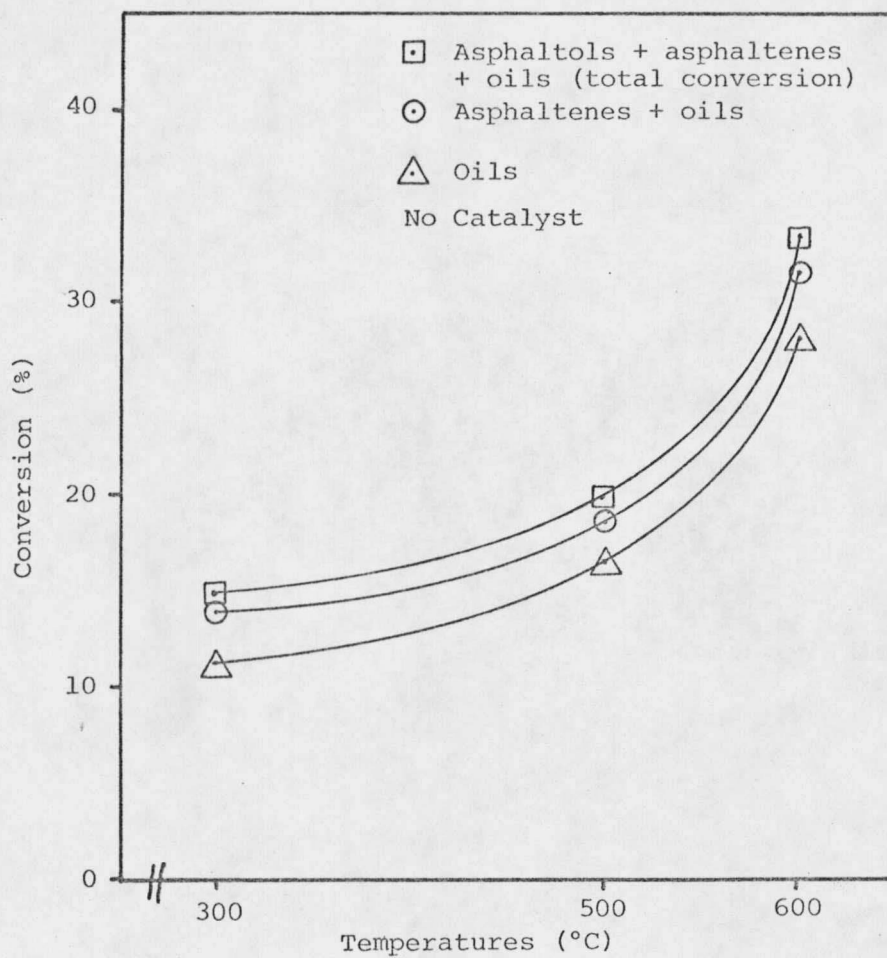


Figure 11. The Effect of Temperature on Coal Conversion

D. The Effect of Hydrogen Flowrate on Coal Conversion

The effect of gas flowrate on coal conversion is given in Figure 12. Increased hydrogen flowrate decreased conversion with all other variables held at the standard conditions. Hydrogen flowrates tested were 8, 10, and 12 standard cubic feet per hour. Decreased conversion would be expected since an increased hydrogen flowrate decreases the amount of time each coal particle spends in the reaction zone. Calculations have been done to determine the hydrogen residence time in the reactor and are presented in Table VI. These calculations are based only upon the flow of hydrogen through the reactor tube and do not account for the presence of the coal in the gas stream.

Table VI. Residence Time Based Upon Hydrogen Flowrate

<u>Hydrogen Flowrate (Std ft³/hr)</u>	<u>Residence Time for 6 ft Reactor (sec)</u>
8	0.21
10	0.17
12	0.14
<u>Reactor Length (ft)</u>	<u>Residence Time for H₂ Flowrate of 8 std ft³/hr (sec)</u>
6	0.21
12	0.42
18	0.63

The results obtained agree with the reports made in the literature. A decrease in conversion for increased hydrogen flowrate is

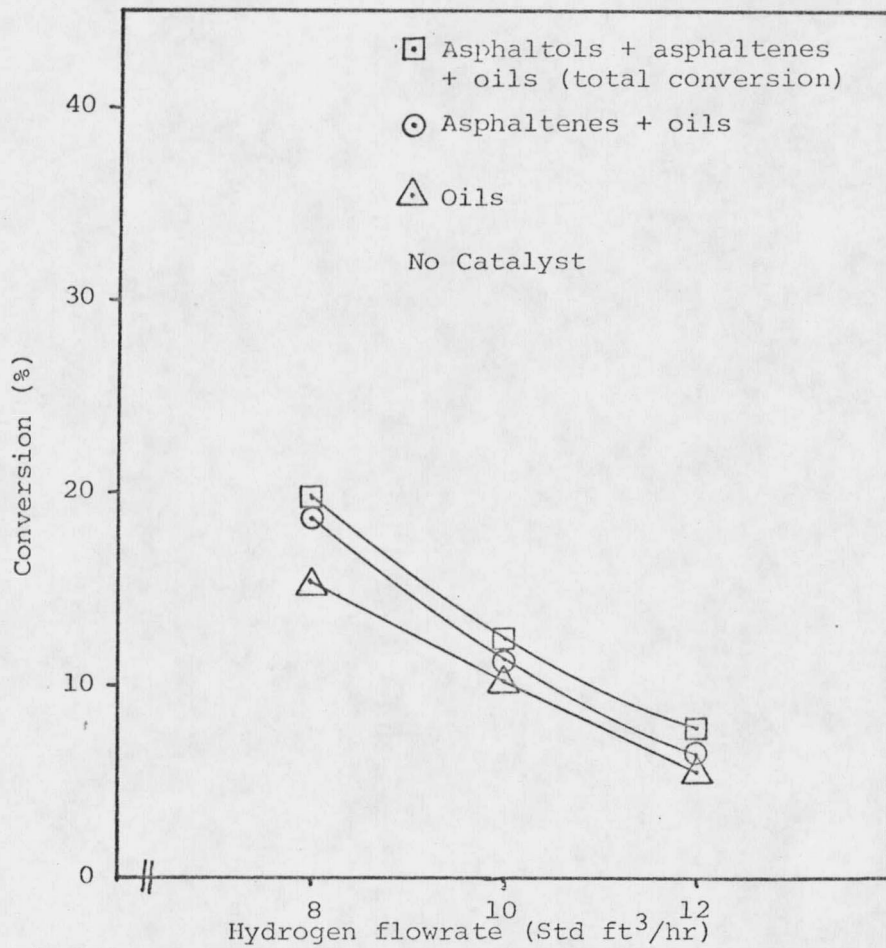


Figure 12. The Effect of Hydrogen Flowrate on Coal Conversion

reported by Wood and Wiser [14]. The same is also indicated in Schroeder's patent [25].

E. The Effect of Reactor Length on Coal Conversion

The three reactor lengths tested in this study were 6, 12 and 18 feet. The results (see Figure 13) did not show any conclusive trends. It is hypothesized that the reason for this was that there was not enough difference between the reactor lengths for any differences in conversion to be detected. Work performed by Lantz did show a decided increase in coal conversion with increased reactor length for 3/16 inch diameter tubes. However, the tube lengths they studied ranged from 20 to 120 feet in length. They report that conversion was increased by 20 to 85% at 538°C and from 10 to 63% at 510°C when reactor length was increased from 20 to 120 feet [26].

Calculations were done to determine the residence time for each reactor length. The results are presented in Table VI. These calculations again are based only upon the hydrogen flow through the tube and do not take into account the presence of the coal. This is only an estimate of the coal residence time in the reactor.

F. The Effect of Coal Feedrate on Coal Conversion

The effect of coal feedrate upon coal conversion is presented in Figure 14. The coal feedrates tested were 1.68, 2.31, and 7.96 grams per hour. The coal feedrate did not seem to have any great effect.

