



Continuous short residence time coal liquefaction using metal chloride-hydrogen chloride catalysts
by John Jay Waterman

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

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Results indicated that the addition of metal chlorides to coal significantly increased the level of coal conversion over non-catalytic coal. The presence of hydrogen chloride in the feed gas greatly increased coal conversion in both catalytic and non-catalytic coals.

The effect of three operating variables on nickel chloride impregnated catalytic coal was also determined. The coal conversion was shown to increase with increasing temperature and pressure, and to decrease with increasing carrier gas flow rate.

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METAL CHLORIDE-HYDROGEN CHLORIDE CATALYSTS

by

JOHN JAY WATERMAN

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Chemical Engineering

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ABSTRACT

A continuous short residence time coal liquefaction process was analyzed for its capability to catalytically hydrogenate pulverized coal, using a metal chloride, hydrogen-chloride catalyst system.

The coal studied was Rosebud sub-bituminous coal from Colstrip, Montana. The process consisted of a continuous coal feeder which delivered coal to an Inconel, tubular reactor which was run between 400 and 600°C and 500 and 1,000 psig. The coal was carried through the reactor entrained in a flow of hydrogen or a mix of hydrogen and hydrogen chloride. Six different metal chloride catalysts were impregnated on coal and tested for conversion. Analysis included coal conversion by hexane, toluene, and pyridine soluble fraction and nitrogen and sulfur determination.

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The effect of three operating variables on nickel chloride impregnated catalytic coal was also determined. The coal conversion was shown to increase with increasing temperature and pressure, and to decrease with increasing carrier gas flow rate.

INTRODUCTION AND BACKGROUND

A. Current Domestic Energy Condition

Energy is the backbone of our modern technical society. Its heavy influence on nearly every aspect of our everyday lives has developed in such a manner that few realized the scope of our dependency until the Arab Oil Embargo of 1973. As we become ever increasingly dependent on foreign crude oil, our country has launched an intense effort to find alternative energy sources. The present unfavorable trade situations with energy-rich Iran and Mexico due to political unrest, stand to intensify this problem. In addition, the United States is also suffering from decreased production of domestic crude oil. The United States supply of crude oil has a huge impact on the world economic situation as is currently depicted by rising inflation, negative balance of trade, and the worldwide devaluation of the U.S. dollar. It can be seen then, that in order for the United States to retain its standard of living and economic independence, it must define alternative energy sources.

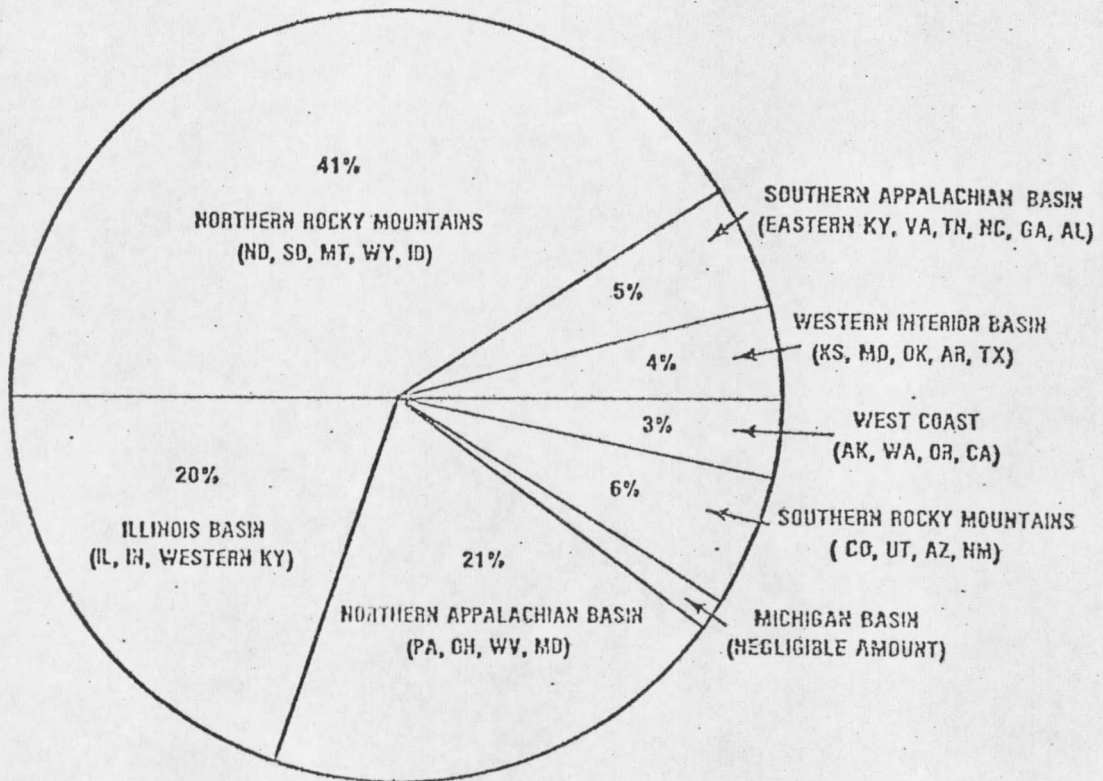
The United States has more energy available on a Btu basis in the form of coal than in petroleum, natural gas, oil shale, and tar sands combined [1]. In light of our current energy shortages, the increased

use of coal to satisfy our needs is essential. However, solid fuel can only be currently applied to a limited portion of our total energy demand while energy use in the transportation, household and commercial areas are totally dependent on liquid and gaseous fuels. In addition, most of the energy consumed in industry comes from liquid and gaseous fuels. Therefore, it would be highly desirable to convert coal to commercial quantities of liquid fuel.

According to figures reported by the 1974 World Energy Council, the United States has about 25 percent of the world's recoverable coal beds [1]. This coal accounts for 94.5 percent of the U.S. fossil reserve [2]. Of the nearly 800 billion tons of coal recoverable from existing coal reserves, almost thirty percent are located in thick beds which are mineable by existing strip mining technology [3]. Figure 1 shows that 41 percent of the demonstrated coal reserve base is located in the Northern Rocky Mountain Region.

B. The Structure of Coal

Coal is a carbonaceous, combustible solid which originated from the accumulation and burial of partially decomposed vegetable matter from previous geological ages [4]. Biological changes and subsequent changes of temperature and pressure altered these deposits of coal such that coal is not a uniform substance and no two coals are the same in



Source: U.S. Geological Survey Bulletin No. 1412.

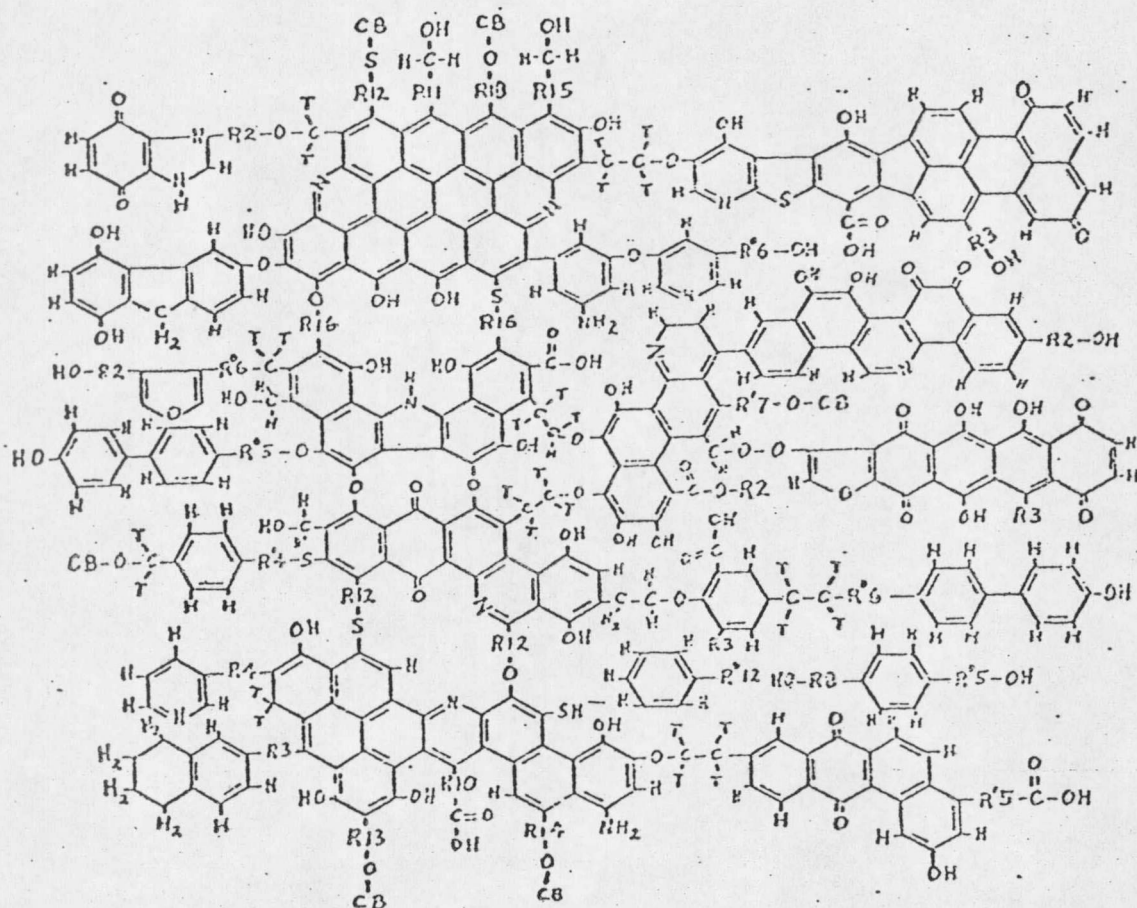
Figure 1. Distribution of Domestic Demonstrated Coal Reserves [1].

every respect. Since increasing geological age buried coal deeper and compressed it more, the depth at which coal is found gives a general guide as to its rank. High rank coals buried deep and mined underground are anthracite and bituminous, while shallower, strip mineable coals are lower ranks of sub-bituminous and lignite. The different ranks have a wide range of composition as well as chemical and physical properties. Coal is primarily composed of carbon, hydrogen, and oxygen with minor amounts of sulfur and nitrogen as well as varying amounts of moisture and minerals.

From chemical characterization work performed on bituminous coals, it appears that long chain, simple aliphatic and alicyclic hydrocarbon groups represent the bulk of the coal molecule. Multiple polynuclear ring structures are apparently absent. Although coals were once thought to have 50 or 60 of the ring structures connected, it appears that only five or six actually combine. A model of the structure is shown in Figure 2 [5].

C. Coal Liquefaction

Coal liquefaction by hydrogenation under pressure at elevated temperatures was first studied by Bergius in 1913. By the 1940's, Germany had nine commercial plants producing liquid fuels from coal. The technology ceased to be developed further due to the then low costs of natural gas and crude oil.



$R^{\circ}N$ 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 2. Typical Structure of Sub-Bituminous Coal [7].

Techniques for converting coal to liquid fuels are now being improved with the current emphasis being placed on the development of fuels suitable for boiler feeds and refinery feedstocks.

Coal has a carbon to hydrogen weight ratio (C/H) ranging from 12 for lignite coals to above 20 for anthracite coal. To convert coal to liquids, it is necessary to increase the hydrogen content of the coal. This hydrogenation process is the result of adding a hydrogen molecule to an unsaturated carbon-carbon bond. If the C/H ratio is lowered to 10, a thick, viscous synthetic crude oil is produced. By increasing the degree of hydrogenation to a C/H ratio of 3, methane gas can be formed.

In the coal liquefaction process, it is believed that the hydrogenation process is accompanied by the decomposition of large molecular weight compounds into smaller fragments [6]. If the coal is heated in a normal pyrolysis process, thermal cracking and polymerization occur with products such as paraffins, olefins, aromatics, tar, coke, char, and polycondensed pitch being formed. If the coal is heated in presence of a catalyst, the amount of polymerization is controlled and more useful products are formed, those being in general alkylated aromatics, liquids and hydrocarbon gases.

It has been reported that as the C/H ratio of the coals increase, the conversion of coal to liquid products decrease, the ideal initial

ratio being 16 [7]. The Colstrip, Montana, sub-bituminous coal used in this thesis work has a C/H ratio of 14.5.

D. Products of Coal Liquefaction

A common means of fractionation and characterization of coal liquefaction products is through a series of solvent extractions. The major classifications of fractions are:

- (1) Oils - hexane soluble fraction.
- (2) Asphaltenes - hexane insoluble, benzene or toluene soluble fraction.
- (3) Asphaltols - benzene or toluene insoluble, pyridine soluble fraction.

Of these, the asphaltene and asphaltol are thought to be responsible for high viscosity and processing difficulties in the various coal liquefaction processes [9].

The oil product is the most desirable since it may be used directly as a feedstock in existing refinery technology. The oils have the highest degree of hydrogenation of the three liquid products.

Asphaltenes are considered to be one of the principal intermediates in the conversion of coal to an oil product.

It has been suggested that asphaltenes are the coal "monomer", that is the smallest unit of coal that still retains the spectral qualities of the whole coal. Additional hydrogenation of asphaltenes to oils is a very

difficult step. In Weller's mechanism of coal liquefaction by the first order series reaction of coal to asphaltene followed by asphaltene to oil, he reported the rate constant at 400°C of the first reaction to be twenty-five times greater than the second or oil producing reaction [10]. Asphaltenes have been shown to have hydrogen bonded acid-base complexes with separate species having only an acid or a base character [11]. It has been concluded that most of the oxygen in asphaltenes are tied up in phenolic hydroxyl groups and about one-fourth of the active hydrogen is associated with nitrogen heteroatoms. There is still a question as to the exact chemical functionality of asphaltenes [12].

Asphaltols appear to be very highly functional polyphenols with more than ten percent heteroatoms. They have a greater basicity and higher oxygen content than asphaltenes. They have also been shown to cross-link and polymerize very readily [11]. It has been shown that for low conversion of coal, the asphaltol product represents up to 80 percent of the total product [9, 13]. The term asphaltol was originally proposed due to the evidence showing that asphaltols could be distinguished from asphaltenes by a higher degree of functionality in the form of more hydroxy groups per molecule [9, 13].

In order to find a more fundamental understanding of the chemical nature of coal liquefaction products, Mobil Research and Development Corporation developed a method of chemical fractionation [13].

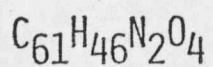
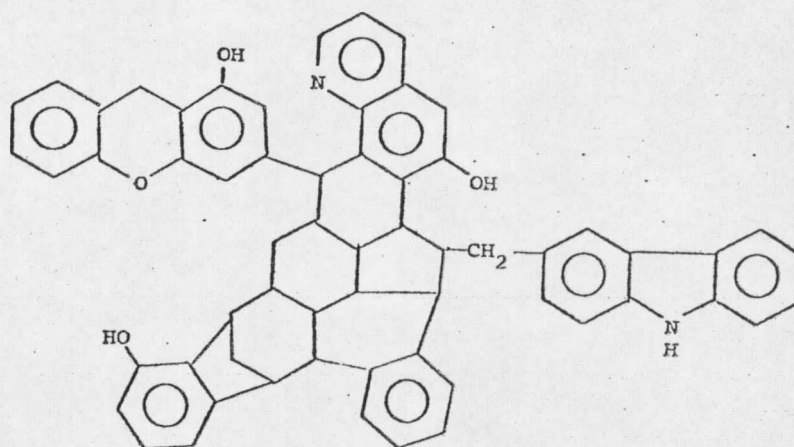
Their basis was that extraction told little about the liquefaction products from a chemical standpoint since solubility depends not only on molecular weight, carbon skeleton, and chemical functionality, but also interactions with other soluble species which can also act as solvents. They postulated that depending on the presence or absence of other species in coal liquid, a molecule could end up as either an oil or asphaltene. The method developed was a liquid chromatographic procedure using silica gel as the stationary phase [14]. The elution solvents, apparent chemical classes, and extraction classification is shown in Figure 3. It is shown that oils contain some non-hydrocarbon compounds which are primarily ethers, and that asphaltenes are for the most part monofunctional. Mobile also reported that the weight percent of heteroatoms in the oil fraction is about 1 percent or less while about 2 percent in asphaltenes and 10 percent in asphaltols. As a result of the Mobil work, a model was developed for the average chemical structure of an asphaltol molecule generated from West Kentucky coal (Figure 4), the structure for the average compound coming from the solution eluted in tetrahydrofuran.

MOBIL FRACTIONATION PROCEDURE

<u>Classical Description</u>	<u>Fraction</u>	<u>Elution Solvent</u>	<u>Major Compounds</u>
Oils (1-3)	1	Hexane	Saturates
	2	Hexane/15% Benzene	Aromatics
	3	Chloroform	Polar aromatics; non-basic N, O, S-heterocyclics
Asphaltenes (3-5)	4	Chloroform/10% Et ₂ O	Simple phenols
	5	Et ₂ O/3% EtOH	Basic nitrogen heterocyclics, di and triphenols
	6	MeOH	Highly-functional molecules (greater than 10% heteroatoms)
Asphaltols (5 thru 9)	7	CHCl ₃ /3% EtOH	Polyphenols
	8	THF	Increasing O content and nitrogen basicity
	9	Pyridine	
	10		Non-eluted, unknown materials

10

Figure 3. Mobil Fractionation Procedure.



73% AROMATIC CARBON

900 MOL. WT.

60% AROMATIC HYDROGEN

Figure 4. General Structure of Average Asphaltol Molecule [13].

E. Coal Liquefaction Processes

The production of liquids from coal can be done by four general methods:

- (1) Hydroliquefaction.
- (2) Solvent extraction.
- (3) Pyrolysis.
- (4) Liquid hydrocarbon catalytic synthesis.

Hydroliquefaction is the direct catalytic hydrogenation of coal under elevated pressure and temperature. In the general process, coal is slurried with a coal derived recycle oil and then mixed with gaseous hydrogen and fed into a reactor run at about 850°F and from 2,000 to 4,000 psig. One of the best catalysts appears to be cobalt molybdate. The main product of this process is a heavy oil, and the coal heteroatoms (sulfur, oxygen, and nitrogen) leave as low molecular weight gases. An example of hydroliquefaction includes the first commercial process for converting coal to liquids. The Bergius process generated gasoline and middle oils for Germany during World War II at a peak production of 64,200 barrels per day. This process operated at 800°F to 900°F and 250 to 700 atmospheres using an iron sulfate-sodium sulfide catalyst. The Synthoil process developed by the U.S. Bureau of Mines is also a hydroliquefaction process. In this method, a synthetic crude oil with a heating value of 17,000 Btu/lb is generated at a yield of 3.3 barrels per ton of coal. The sulfur content is still fairly high,

almost 0.3 weight percent in the product. Cobalt molybdate catalyst impregnated on a silica promoted alumina support is used to catalyze the reaction at 850°F and 4000 psig. Other examples of hydroliquefaction include the Co-Steam process, H-Coal process, and various Zinc-Chloride Catalyst processes [15, 16].

Solvent extraction is the liquid phase dissolution of coal to liquids. In this method, the coal is partially dissolved in a hydrogen rich solvent and the undissolved portion is filtered out. The solvent is recovered from the product by distillation while the undissolved solid is reacted with steam to produce hydrogen. These processes are generally termed as solvent refined coal (SRC).

The Exxon hydrogen donor solvent process and the Cresap SRC process are examples of the solvent extraction process. In the Exxon method, a hydrogenated hydroaromatic material is used as the donor solvent at operating conditions of 850°F and 200-1000 psig. They are operating a one-half ton per day pilot plant in Baytown, Texas. The Cresap SRC process runs at 765°F and 150 psig. Flour Engineering is operating a 20 ton per day pilot plant at Cresap, West Virginia. The Cresap process is also called Project Gasoline. Generally the liquid products of SRC processes must be upgraded by catalytic hydrogenation [17]. Other SRC processes include the Pamco Process, Southern Services SRC Process and Solvent Refined Lignite Process [15, 16].

Pyrolysis of coal in the most general sense is the heating of coal in the absence of oxygen and hydrogen to crack the large molecules into smaller liquid and gaseous products. In this process, most of the carbon is rejected as a solid char. The liquid products must be further upgraded to be in a usable form. Examples of coal pyrolysis are the FMC COED process and Oil Shale Corporation's Toscoal Process. In the COED method, coal is heated using successively higher temperatures in a series of four fluidized bed carbonizers. Process pressures are from 5 to 10 psig while process temperatures range from 500°F in the first carbonizer to 1600°F in the fourth stage. A 36 ton per day COED pilot plant has been successfully run in Princeton, New Jersey. The plant has now been dismantled. In the Toscoal process, crushed coal is preheated in a fluid bed and then fed to a pyrolysis drum where it is heated by hot ceramic balls. Pyrolytic vapors are condensed and fractionated. Operating temperatures are from 800°F to 1000°F. A 25 ton per day pilot plant has been run using Wyoming sub-bituminous coal. Other pyrolytic processes include the Hydrocarbonization process, Seacoke process, and Garrett Coal Pyrolysis Process [15, 16].

Liquid hydrocarbon catalytic synthesis can be achieved using synthesis gas via the Fischer-Tropsch method. In this process, coal is converted by gasification to synthesis gas (hydrogen and carbon monoxide) which react in the presence of a Fischer-Tropsch catalyst

to produce a variety of liquid products. The yield depends on operating conditions and choice of catalyst. Methanol can be produced exclusively by choosing copper-zinc-chromium catalysts and specific operating conditions. The Fischer-Tropsch process technology has been available commercially for years as evidenced by the SASOL 8,000 ton per day plant operating in South Africa. Here coal is gasified via the German Lurgi Process and liquid products are generated at 300 to 360 psia and 430 to 660°F [15, 16].

F. Short Residence Time Coal Liquefaction

Research studying the rapid coal liquefaction using short residence time is being studied at several locations around the United States. The research is generally divided into two general categories: (1) noncatalytic flash hydrolysis (FHP) and (2) rapid catalytic hydrogenation.

The basis of this research comes from the premise that in the rapid heating and hydrogenation, the formation of high boiling tars and char is partially eliminated. Only a short period of time is apparently required for the liquefaction of coal; and if the liquefaction products are held at elevated temperatures for longer periods of time, no additional conversion is obtained. In fact, the amount of useful products decreases through polymerization and form less useful products such as char (Figure 5) [11]. Research performed at Pennsylvania State University shows that coals generate the most volatile matter yield if

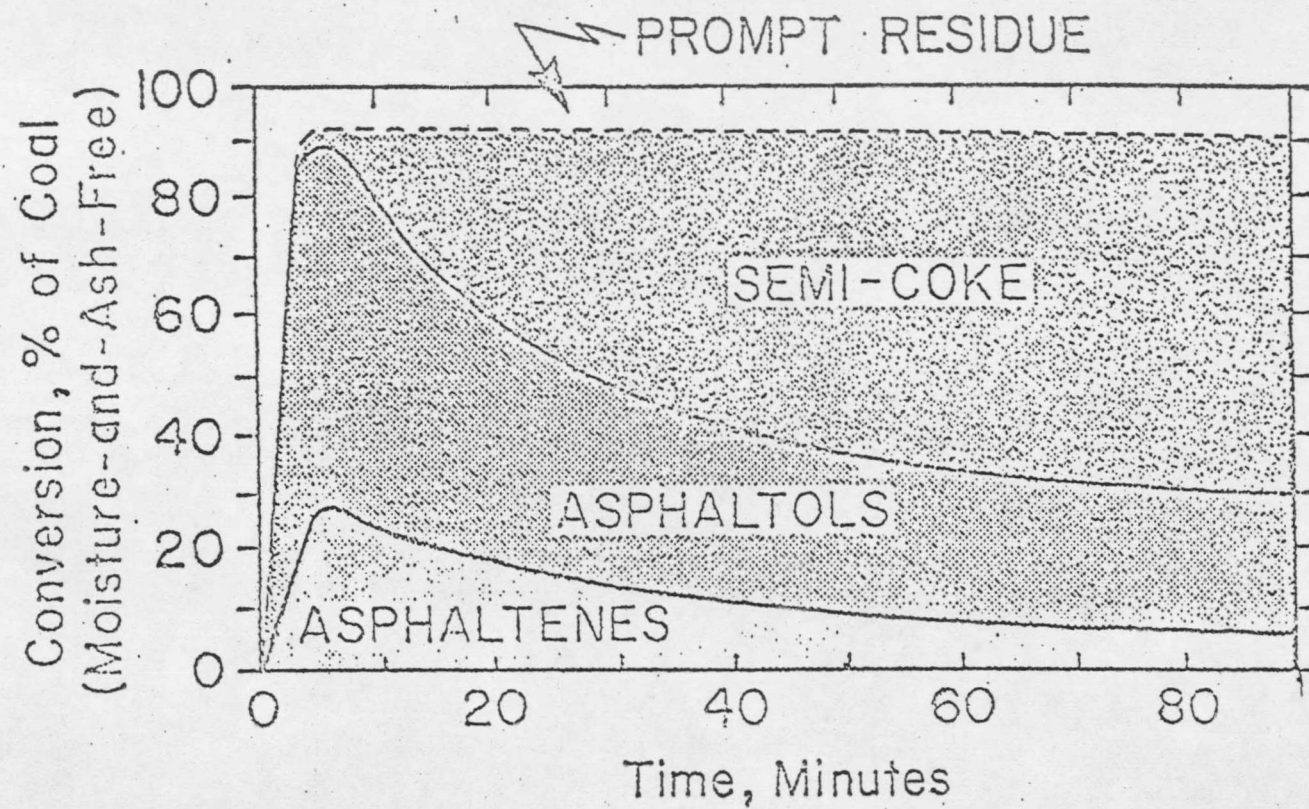


Figure 5. Conversion of Coal vs. Time of Reaction.

heated to reaction temperatures at extremely high rates. It appears these high rates prevent cross-linking polymerization which reduces the yields of the desirable products [18, 19].

Short residence time (SRT) coal liquefaction is a fairly new technology in which coal is rapidly hydrogenated at high temperature and pressure and then quenched to yield a variety of products including substitute natural gas, an aromatic distillate oil composed of mainly benzene, toluene, and xylene, a fuel oil, sulfur, ammonia, and char. Residence times are generally fractions of a second.

A mechanism has been proposed for the hydropyrolysis of coal in which it is postulated that in the initial stages, decomposition reactions occur as a first order conversion of carbon solids to volatile species that flow out of the solid into the bulk gas flow. Since this flow is high, there is little chance for hydrogen to reach the solid interface and react directly. In the bulk phase, the volatile products of coal decomposition react further with the hydrogen. At high temperatures, molecular cracking can occur and free radical products are stabilized by the high excess of hydrogen present. Thus alkylated aromatics would be dealkylated to form benzene and methane and result in a high yield of the desirable oil product. At lower temperatures, the molecular cracking would occur to a lesser extent and more alkylated species such as toluene, xylene, phenols, and naphthalenes would be in the product [20, 21].

RELATED RESEARCH

A. University of Utah's Continuous Coal Hydrogenation Process

The University of Utah has developed a continuous catalytic flash hydrogenation process utilizing a tubular reactor system feed by a star wheel feeder. This design uses a high velocity, turbulent flowing hydrogen stream to entrain pulverized coal and carry it through a pressurized and heated tubular reactor. The process emphasizes short residence time and short hydrogen to coal ratios.

The process equipment consists of a pressurized dual coal hopper and rotary wheel feeder, a hydrogen-coal particle preheater, a tubular reactor, a solids-liquids receiver, condensers, a filter, and sampling and monitoring devices. The system can operate at 2,000 psi at a coal feedrate from 3 to 500 grams per minute. The preheater and first reactor section are immersed in molten lead while a furnace heats the remaining part of the reactor. The reactor consists of 20-foot sections of coiled tubing. Residence time is varied by choice of reactor length. A typical run consists of a coal rate of 100 g/min at a hydrogen flow rate of 30 standard cubic feet per minute with -40 mesh coal impregnated with 5.5 percent dry zinc chloride at a temperature of 550°F and 2,000 psi. They have obtained conversion (MAF) of over 40 percent for these zinc halide catalysts [22, 23, 24].

B. Cities Service Research and Development Short Residence Time
Coal Hydropyrolysis

In the Cities Service FHP process, pulverized coal (70 percent through 200 mesh) is mixed with preheated hydrogen and fed to a reactor at pressures ranging between 600 and 3,000 psig and temperatures ranging between 1100°F and 1800°F. This process is non-catalytic. Coal-particle residence time can be controlled between 0.1 and 2 seconds. After the short reaction, the products are rapidly quenched by flushing with cryogenically cooled hydrogen. The char is separated and the gas stream is cooled to condense benzene-toluene-xylene liquid, oil, ammonia liquor, and water.

The reactor is a free-fall pipe heated by an electric furnace. Coal is fed batchwise into a pressurized hopper where a star wheel feeder delivers the coal and pre-heated hydrogen to the reactor. The coal falls with the hydrogen through a four-foot pipe-reactor devolatilizing along the way. The residence time is controlled by introduction of cold hydrogen through a variable length probe inserted into the bottom of the reactor. This allows for changing the reactor length without changing the reactor. The reactor is a 1½ inch scheduled XX pipe. The condensing system can be varied from -200°F to +200°F by use of suitable coolants. The non-condensable gases are metered, analyzed by gas chromatography, and vented. Table I gives a range of operating conditions which have been studied. With this system,

Table 1. Cities Services Process Run Conditions

Run Time	1.25-8.0 Hr
Hydrogen/Coal Ratio	0.18-2.0 lb/lb
Avg. Particle Size	50-40 microns
Coal Heatup Rate	50,000-150,000 °F/sec
Avg. Reactor Temperature	1150-1575°F
Reactor Pressure	500-3,000 psi
Quench Temperature	450-1000°F

Cities Services can process up to two pounds of coal per hour and have routinely achieved coal conversions of 50 to 80 percent [25, 26, 27].

An economic analysis of a scaled-up commercial plant using this process indicates that a 14,124 TPD coal plant will consume 838 TPD of hydrogen while producing 3,030 TPD methane, 840 TPD ethane, 982 TPD benzene-toluene-xylene liquid, 1,463 Tpd carbon monoxide, 129 TPD ammonia, 2,265 TPD water, and 6,072 TPD char. The cost of such a plant is estimated (1st quarter, 1977) to require a \$1.2 billion capital investment and 88 million in annual operating costs. The gas price has been preliminarily estimated to be between \$2.66 and \$3.09

per million Btu for \$5.00 per ton of coal. This compares with \$3.49 per million BTU for the Lurgi process.

C. Spencer Chemical Company Process

The Spencer Chemical Company FHP process is a rapid catalytic hydrogenation method for converting coal to liquids. Pulverized coal is hydrogenated at temperatures ranging from 900°F to 1000°F and 1,500 to 2,000 psi with a residence time of less than one minute. The main product is a crude aromatic oil which can be further refined to gasoline and light oils by conventional techniques. Catalytic coal and preheated hydrogen are fed continuously into a reactor where hydropyrolysis occurs. The products are cooled rapidly and then separated. The method of feeding was assumed to be either star wheel type or screw type and the catalyst type and amount are proprietary. A material balance based on a scaled-up plant indicated that a plant using 14,840 TPD of coal and 325 TPD of hydrogen, would produce 1,610 TPD of gas (heating value = 780 Btu/scf), 8,383 TPD crude oil, and 1,840 TPD of ash and char. Preliminary economics indicate this plant would require a capital investment of \$205 million at an annual operating cost of \$30 million. For \$10/ton of coal at 15 percent return on investment, this is \$1.36 per million BTU [28].

D. Brookhaven National Laboratory FHP Process

Researchers at Brookhaven National Laboratories are studying the process variables and chemistry of a rapid gas phase, non-catalytic flash hydropyrolysis process. The bench scale experimental equipment is composed of a one-inch down flow entrained tubular reactor designed to be operated at pressures up to 4,000 psi and temperatures of 900°F with a coal feed of two pounds per hour and hydrogen feed of one pound per hour. Originally coal was fed to the reactor with a rotating cavity type feeder. However, a screw type has recently been installed and used with better success. It was reported that the hydrogen preheater constructed from Inconel 601 had ruptured after 18 hours of use at 3,000 psi due to hydrogen embrittlement. The preheater was replaced with Inconel 617 and has functioned over 100 hours with no problems.

Experimental results show that hydrocarbon yields increase to 60 percent with pressure up to about 3,000 psi. At 750°C about one-third of the yield is liquid while at 800°C the yield is essentially all methane. At 3,000 psi and 800°C, gaseous product yield increases and liquid product yield decreases as the residence time is increased from 2.3 to 9 seconds. Further tests show that at 750°C, some decomposition of the liquid product (benzene-toluene-xylene) occurred as residence time exceeded seven seconds. As the reactor temperature

increased, both the rate and extent of the liquid decomposition increases. Studies performed on sub-bituminous coal rather than lignite showed similar product analysis except the increase of ethane in the gaseous product with sub-bituminous coal [29, 30].

E. Institute of Gas Technology Riser Cracking of Coal Process

In the Riser coal cracking process, non-catalytic coal is metered through a continuous feeder into a hydrogen carrier gas stream. The mixture is preheated by radiantly heated coal to 1200°F. The mixture then enters the riser reactor tube and moves upward. Air or oxygen is injected into the reactor and ignition takes place. The combustion supplies the heat for the cracking reaction. The combustion takes place in a turbulently flowing region rather than a flame and thus is completed within a few inches of the oxygen inlet. At the end of the reactor, nitrogen is bled in to insure combustion ceases and to cool down the products. The reactants are then carried to a separator where char is disentrained. A water chilled condenser then separates out the liquid products and the gases are analyzed by on-line gas chromatography.

A bench scale unit has shown that carbon conversion increases uniformly with increases in severity of thermal treatment. Also the weight

fraction of char decreases uniformly while weight fraction gases and liquids increase uniformly with increasing severity of thermal treatment. The weight fraction of gases increases more sharply than that of liquids. The unit has been run predominantly at 1800°F and 2,000 psi, yielding synthetic natural gas. However, it has been shown that lower temperature pyrolysis results in production of liquid products.

Currently a larger scale design is being finalized to produce fuel gases, fuel oil, and high octane motor gasoline from a unit processing 100 lb/hr of lignite coal and 12 lb/hr of hydrogen at a temperature of 1500°F and pressure of 2,000 psig. The experimental investigation will dwell primarily on changes in operating pressure and residence time [21].

Due to mechanical problems such as bridging and sticking in devices such as star wheel feeders and screw feeders, a novel method of feeding the coal continuously to the reactor was developed. The method used was to aerate the solids and meter them into the main transport line by entrained flow through a small diameter orifice (Figure 6). Coal is channeled into a plenum chamber by a funnel at the bottom of the coal hopper where it is entrained in a flow of gas moving through the plenum chamber into a one-eighth inch diameter orifice and emptying into the one-eighth inch diameter main transport line.

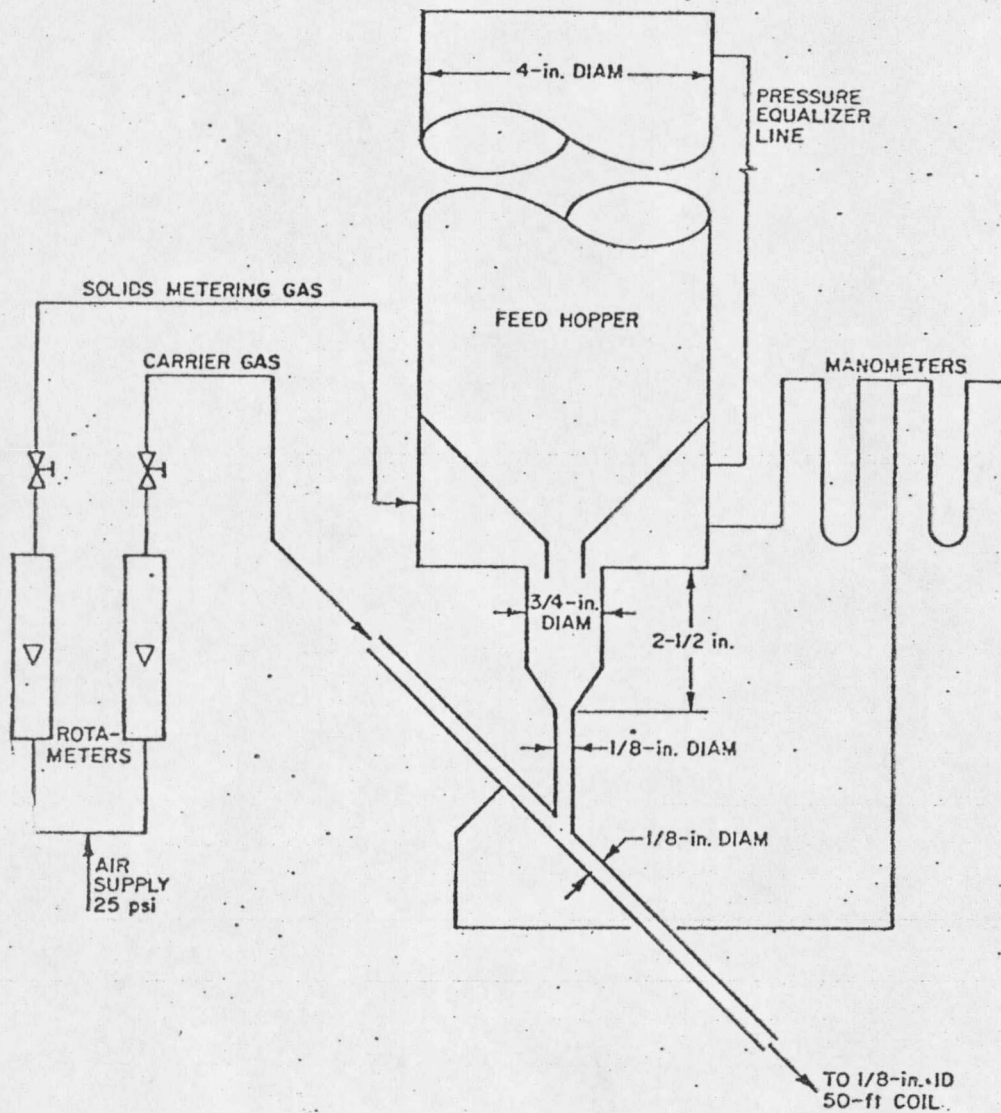


Figure 6. Institute of Gas Technology Solid Feeding System [21].

Problems encountered with the system were mainly due to sticking due to static electricity. When the coal was treated with an anti-static agent, the problem was greatly diminished. The feedrate was correlated nicely to the square root of the superficial gas velocity in the exit port. Uniform and reproducible feedrates are produced with many different mesh sizes of lignite coal [31].

F. Rockwell International Partial Liquefaction FHP Process

The Rockwell-Rocketdyne coal liquefaction process is based on the premise that high liquid yields can be obtained by rapid mixing, rapid quenching, flash pyrolysis. Pulverized non-catalytic coal is injected into the reactor in a method similar to the Institute of Gas Technology approach. However, a rocket engine is used as the injector. This method provides for extremely high mixing, thus reducing the problem of insufficiently reacted coal. The coal is mixed with hydrogen preheated to 1200°F. Reaction residence times can be varied from 10 to 1,000 milliseconds at temperatures ranging from 1500 to 1900°F and pressures of 500 to 1,500 psig. The reaction products are quenched with a water spray.

Phases involved in this study include a one-fourth ton per hour, one ton per hour, and ten tons per hour processes. Overall carbon conversions are on the order of 50 percent, 40 percent being liquid

products. Conversions as high as 64 percent have been achieved. A detailed two phase flow model of the rocket engine injection feeder method has also been done [32, 33].

G. Occidental Research Corporation Flash Pyrolysis System

The Occidental Research Corporation's flash pyrolysis system has undergone several bench scale phases and is currently operating as a three ton per day coal capacity process development unit. The process consists of feeding milled non-catalytic coal by means of a screw feeder into a pyrolysis reactor at rates up to 300 pounds per hour. The coal is then mixed with hot recycle char which heat the coal up rapidly to around 1200°F. The char recycle rate is from five to ten times the coal feed rate. After initial heatup, process heat is generated by combusting some of the recycle char. Pyrolytic vapors are separated from the char in a series of cyclones. A vacuum flash unit is used to recover the liquid products. No hydrogen is used in the process. Catalytic hydrogenation methods are being studied to upgrade the tarry liquid products.

Current results show that the process is technically viable over extended periods of time. Tar derived from the unit show significant amounts of benzene-toluene-xylene liquids and phenols. A theoretical model was developed for the devolatilization and cracking of the coal [34, 35].

H. Other Research

Other short residence time coal liquefaction is being done at the City University of New York, Pittsburg Energy Research Corporation, and Mobile Research and Development Corporation [27, 38].

I. Montana State University Research

Previous research at MSU has shown metal chlorides to be active hydrodenitrogenation catalysts in the presence of hydrogen chloride gas for treating heavy California gas oils [36]. This concept was then applied to the batch hydrogenation of Montana sub-bituminous coal. Several metal chloride catalysts impregnated on pulverized coal were screened for hydrogenation activity [8, 37].

A continuous tubular reactor system was designed and built using the short residence time flash hydropyrolysis principle of coal liquefaction. The effects of temperature, pressure, and flowrate on the conversion of untreated coal in a hydrogen atmosphere were determined. Also the effect of three metal chloride catalysts on the conversion of coal in a hydrogen atmosphere was determined [7].

The basis then of this research is to use the dual functional catalyst capabilities, i.e. acid to catalyze cracking and metal to catalyze hydrogenation, of the metal chloride-hydrogen chloride system in the continuous short residence time liquefaction of Montana sub-bituminous

coal. It is hypothesized that this system will result in a high conversion of coal to liquid and gaseous products.

Advantages of this system are:

- (1) Short residence time hydrolysis gives high conversion of hexane soluble liquid product.
- (2) The process equipment is inherently simple.
- (3) Asphaltene products can be minimized.
- (4) The catalyst system is active in nitrogen removal.

RESEARCH OBJECTIVES

The objectives of this research were:

- (1) To obtain reliable and reproducible coal feedrate data from a continuous star wheel feeder.
- (2) To screen six different metal chloride catalysts using the continuous short residence time coal liquefaction process. The criterion of conversion will be used to characterize the catalysts in both hydrogen and hydrogen-hydrogen chloride feed gases.
- (3) To further characterize the catalysts' effectiveness by analyzing liquid products for nitrogen and sulfur.
- (4) To determine the effect of pressure, temperature, and carrier gas flow rate on coal conversion.

MATERIALS, EQUIPMENT, AND PROCEDURES

A. Process Description

Pulverized coal is charged batchwise to a coal feeder where it is continuously fed by a rotating star wheel feeder to a coiled tube reactor. In the feeder, the coal is entrained in the flow of a carrier gas which propels the coal through the reactor. The product is collected in a collection vessel and the gas flow is depressurized, metered, and vented to the atmosphere. Since it was proposed to use gaseous hydrogen chloride mixtures as a carrier gas, all internal equipment parts were made of Inconel whenever possible for resistance to corrosion. A process flowsheet is shown in Figure 7.

B. Coal Star Feeder

A rotating coal star feeder was obtained from W. D. Peterson and Associates of Murray, Utah (Figure 8). The feeder was equipped with a star shaft consisting of three cubic centimeters of volume per revolution. The feeder shaft was driven by an electric motor with a variable speed output which allowed the shaft speed to vary from 0.2 to 3.3 revolutions per minute (Figure 9) [7]. The feeder and hopper unit were made of Inconel for corrosion resistance.

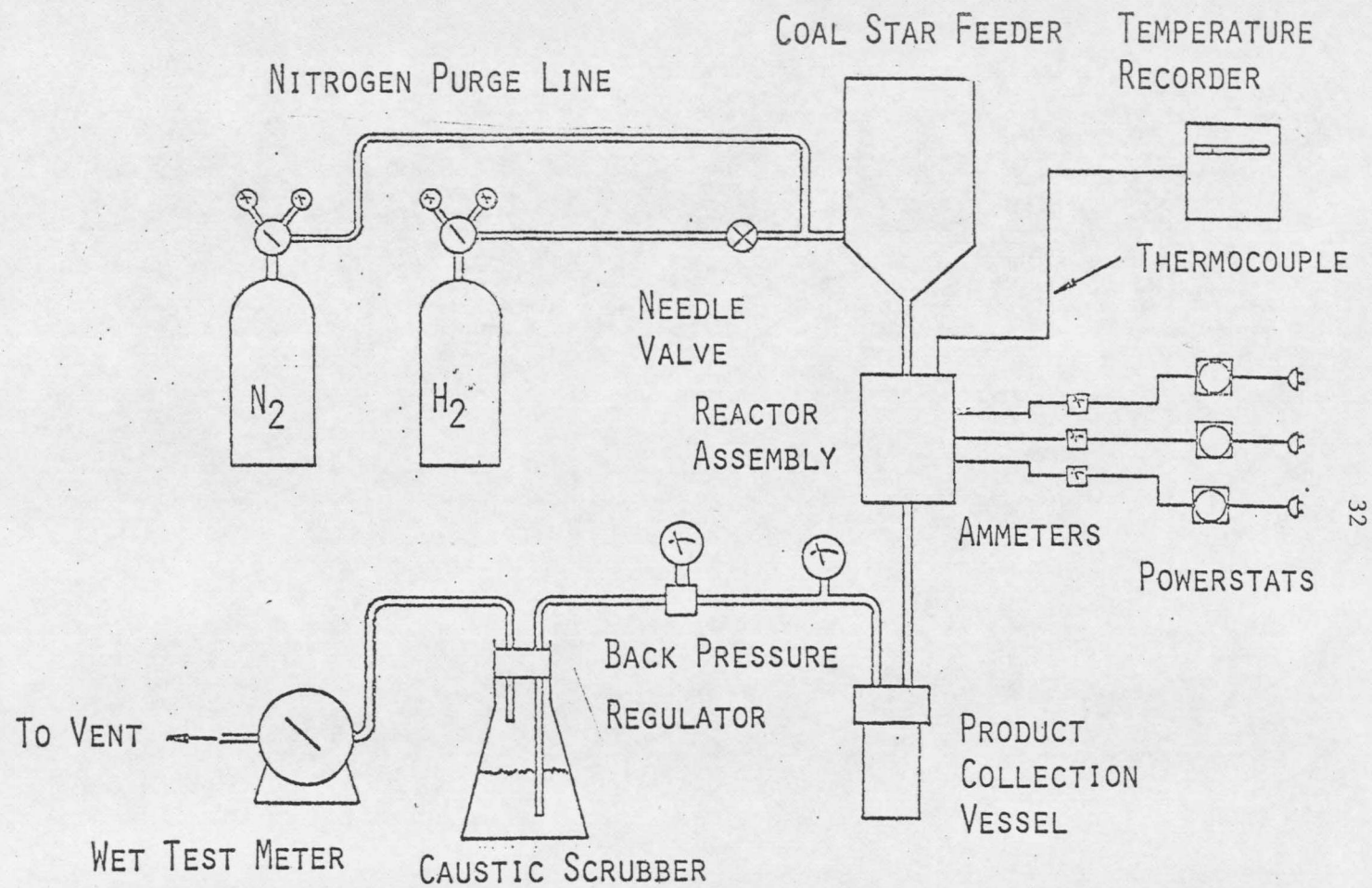


Figure 7. Process Flow Diagram

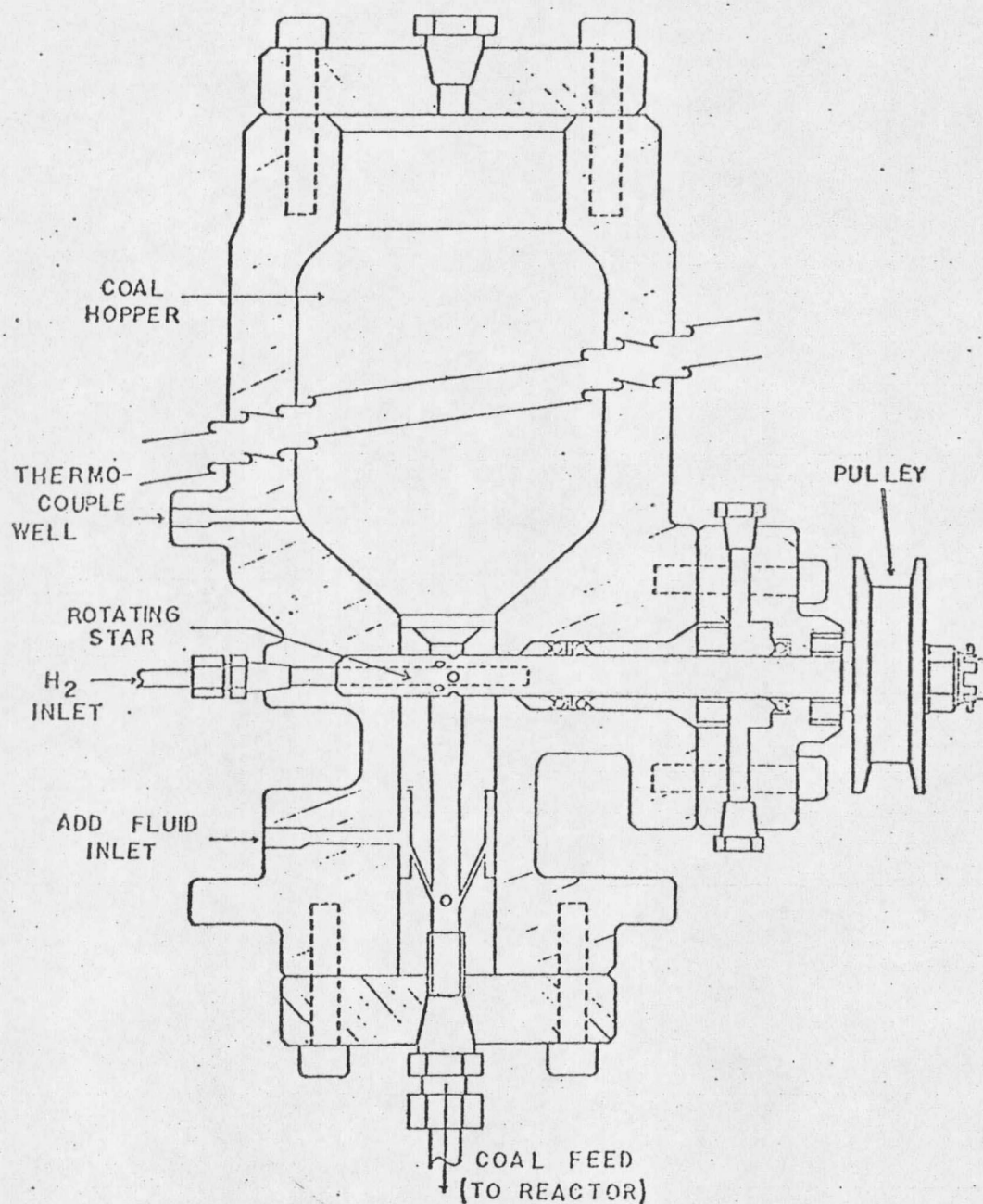


Figure 8. Coal Star Feeder.

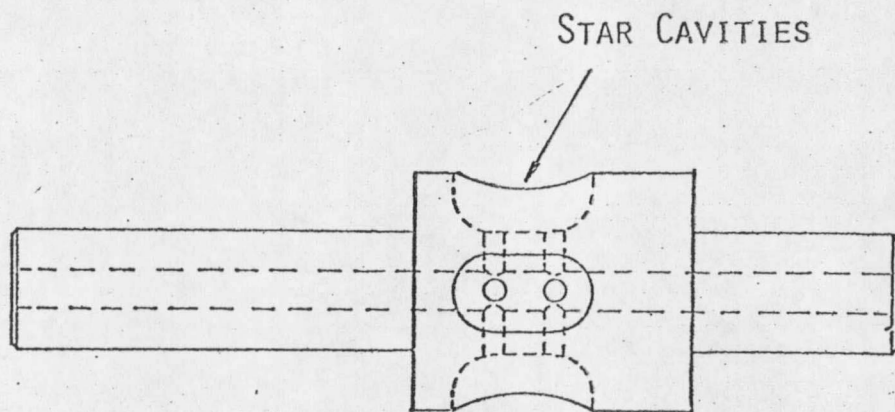


Figure 9. Three Cubic Centimeter Star Shaft.

C. Reactor and Heater Assembly

The reactor used in this research consisted of a length of $\frac{1}{4}$ -inch Inconel 617 tubing, ten feet long. The reactor was coiled around a $3\frac{1}{4}$ ", $\frac{1}{2}$ " wall, stainless steel pipe. The heavy walled pipe was used to provide an approximately constant temperature heat source for the reactor. The reactor was externally insulated with about six inches of zonalite insulation (Figure 10).

Process heat was supplied to the heavy walled stainless steel pipe by an immersion type strip heater that fit inside of it. Power was supplied to the strip heater by powerstats connected to 110 volt wall plugs. In-line ammeters measured the current going to each of the three strips of the heater. Heatup time for this system was about one-half hour to bring the reactor temperature up to 500°C.

D. Product Collection and System Pressure

The products were collected in a Parr Series 4000 pressure reaction apparatus which was modified to accept $\frac{1}{4}$ " Swagelock fittings. This vessel is rated by the manufacturer to be sound to 10,000 psi. The copper head gasket and autoclave head were secured using a torque wrench. New copper head gaskets were torqued to 60 ft-lbs and upon subsequent runs were torqued higher in 10 ft-lb increments until 100 ft-lbs was reached, whereupon a new gasket was installed. Silver

FROM STAR FEEDER

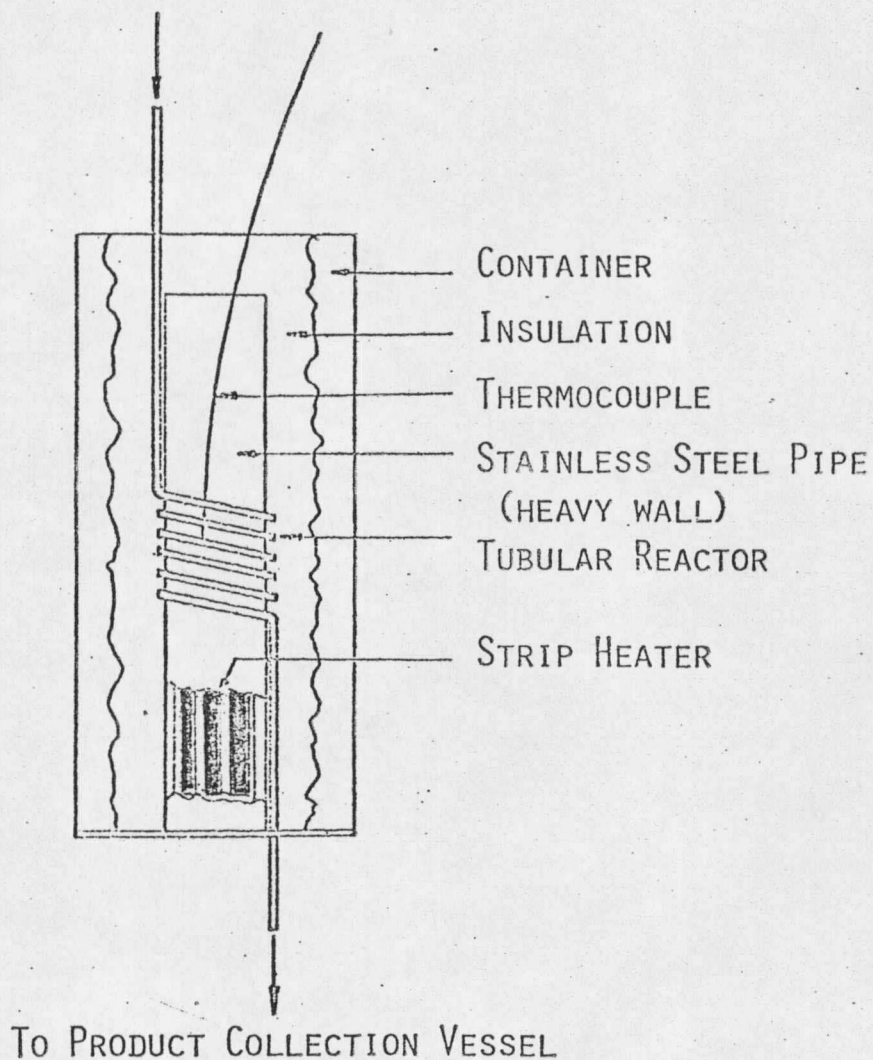


Figure 10. Reactor and Heater Detail.

Goop was used on the autoclave cap bolts to prevent seizure at high temperatures.

The system pressure was maintained by a Grove Mighty Mite back pressure regulator. The internal parts of this device were re-machined from Inconel for the purpose of corrosion resistance. A teflon diaphragm was used in the pressure regulator.

E. Temperature Measurement and Hydrogen Flow Measurement

The reactor temperature was measured using a chromel-alumel thermocouple connected to a single point Honeywell temperature recorder. The thermocouple was attached to the outside wall of the Inconel tubular reactor (Figure 7).

The technical grade hydrogen gas was supplied from commercially obtained, regulated gas cylinders. The hydrogen chloride gas mixes were prepared as needed. Hydrogen chloride was allowed to flow into an evacuated cylinder until the desired static pressure was reached. The cylinder was then pumped with hydrogen to the desired total pressure with the aid of a Haskel Gas Booster air-driven compressor.

The gas flowrate was controlled by a micrometer valve and measured downstream by use of a wet test meter.

F. Preparation and Analysis of Coal

Coal used in this study was Rosebud, Montana, sub-bituminous coal supplied by Western Energy Company in 1975. The coal has been stored in plastic lined drums to prevent any decomposition. Table II gives the proximate and ultimate analysis of the coal. The carbon to hydrogen ratio is about 14.5.

The coal used in the research was taken from the drums and pulverized in a ball mill. The coal was then screened to -60 mesh. This coal was then stored in polyethylene bags to await use. The coal was not screened further and it was decided to use the total -60 mesh coal rather than any fraction of it [7].

All coal samples used in this research were predried for forty-eight hours before being charged to the coal hopper. The drying was done in a forced air oven at 100°C. The purpose of the drying was to improve the feeding characteristics of the coal [7, 19, 26]. All coal samples were treated in a similar manner to prevent any possible alterations of composition between samples.

Table II. Analysis of the Colstrip Sub-bituminous Coal.

<u>Proximate Analysis</u>	
Moisture (as received)	23.9%
Volatile Matter (MF)*	40.6
Fixed Carbon (MF)	49.4
Ash (MF)	10.0
 <u>Ultimate Analysis (MF)</u>	
Carbon	66.1%
Hydrogen	4.5
Nitrogen	0.9
Sulfur	0.5
Oxygen	18.0
Ash	10.0
 <u>Analysis of Major Ash Components</u>	
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

Since conversion of the coal was determined on a moisture and ash free basis (MAF), an analysis of the moisture and ash in the coal was required. The moisture analysis was completed implementing the apparatus shown in Figure 11. Toluene and a weighed amount of coal were charged to the boiling flask. As the rising toluene and water vapor condensed, it fell into the graduated receiving arm. Since water has a higher density than toluene, it settled to the bottom of the receiving arm. The equilibrium volume of water present in the receiving arm along with the weight of the initial coal charge allowed the moisture content of the coal to be calculated. This analysis was allowed to run for twenty-four hours to insure that all the water had been stripped from the coal. The analysis was run on fresh coal as well as coal which had been dried for 48 hours.

The ash content of the coal was determined by heating a weighed amount of coal in a covered crucible with a bunsen burner. After the volatile matter had been driven off, the crucible cover was removed and the fixed carbon was burned away. The remaining brownish colored residue was weighed and the ash content of the coal was calculated.

These analyses were done using random samples of pulverized coal and it is assumed that through the ball-mill mixing, representative samples were generated.

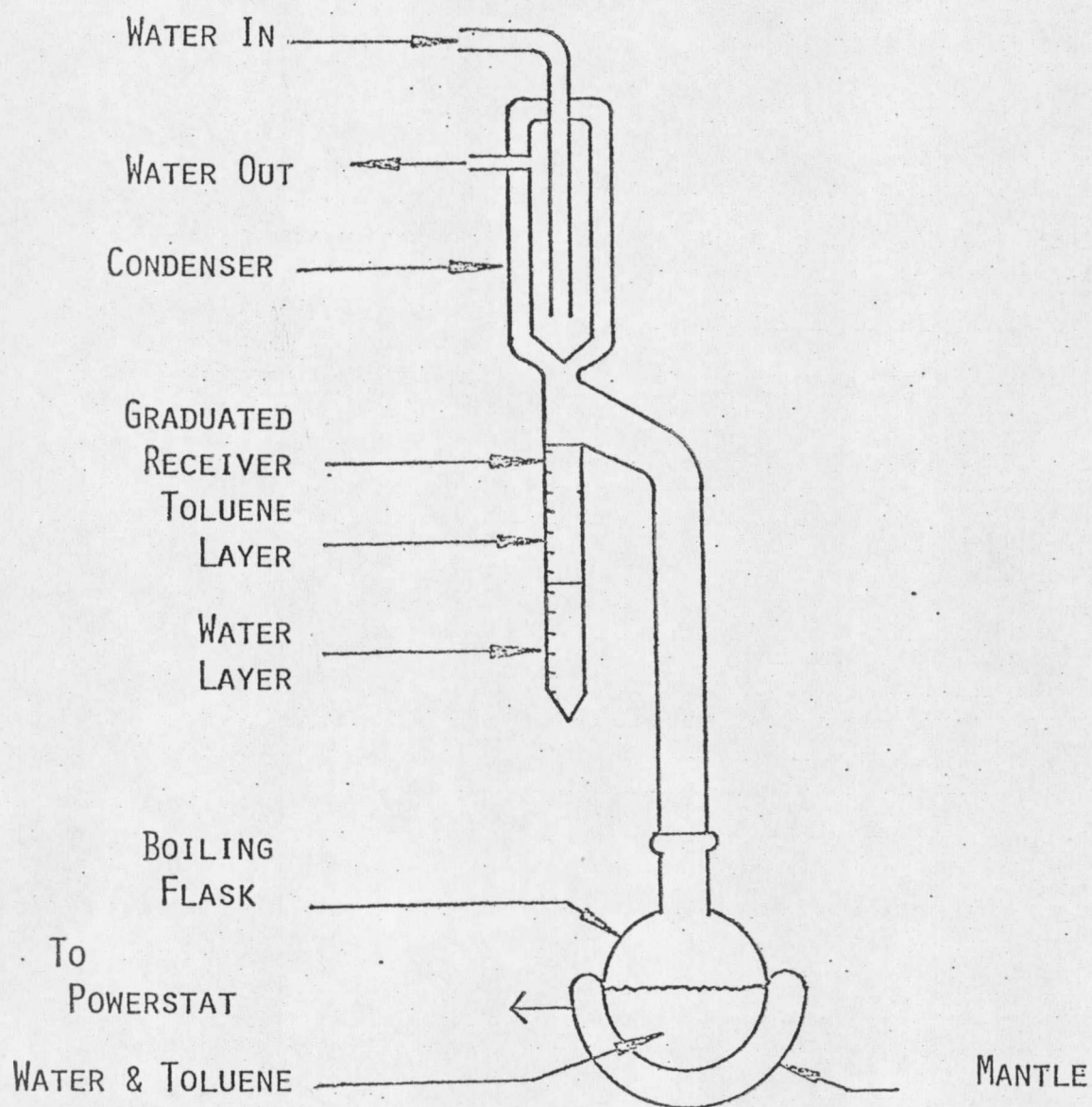


Figure 11. Apparatus Used to Determine Moisture Content of Coal.

G. Preparation of Catalytic Coal

In order to compare the activities of the metal chloride catalysts, they had to be prepared on an equivalent basis. Since previous catalyst impregnation work had been done with nickelous chloride, it was chosen as a reference [37]. It was decided to use approximately 3 weight percent metal on the coal. Three percent nickel was chosen since it was the maximum amount which in aqueous solution would still wet the coal.

The coal was impregnated by adding a weighed amount of predried coal to an aqueous solution of metal chloride. The aqueous solutions were based on the equivalent amounts of metal which would result in a 3 percent metal on coal weight ratio. Once the coal was added to the water solution, agitation was provided until the coal was wetted. The mixture was allowed to stand for twenty-four hours with only sporadic agitation. At this time, the evaporation rate of the water was increased by placing the mixture into a drying oven at 90°C. The mixture was allowed to stay in the oven for forty-eight hours to insure that all the water of hydration associated with the metal chlorides were driven off. The weight gain of the dried coal was attempted to be used to calculate the degree of catalyst impregnation. However, this gravimetric method appeared to be inaccurate. Thus the degree of catalyst impregnation was calculated in a manner similar to the coal ash analysis. A weighed sample of the dried, impregnated coal of known moisture and ash

content was heated in a crucible with a bunsen burner. The volatile matter and fixed carbon were burned off leaving a residue which contained only ash and metal chloride. Knowing the amount of ash, the percent of metal chloride and thus metal on the coal could be calculated.

The six most active metal chloride catalysts reported by Sire in 1975 were used to impregnate coal samples [37]. Those were nickelous chloride hexahydrate, stannous chloride pentahydrate, cupric chloride dihydrate, cobalt chloride hexahydrate, ferric chloride four-hydrate, and zinc chloride. All were technical reagent grade supplied by Fischer Scientific Company.

H. Procedure for Performing a Test Run

A test run was started by charging the coal feed hopper with an amount of predried coal. It was found that samples exceeding 1,000 grams resulted in the most reproducible feed rate data. It was also found that the coal feeder must be kept very clean to get reproducible feedrates. This was done by frequently cleaning the hopper and rotating star shaft. Best results were obtained when the hopper was cleaned at least every other run. The cleaning procedure involved vacuuming out excess coal from the previous run, and then the shaft was cleaned by running acetone and/or toluene through the feeding mechanism. The reactor system was not attached to the feeder during

this solvent cleaning. The solvent was removed by blowing compressed air through the system and then allowed it to air dry overnight.

After the coal was charged to the hopper, the system was slowly pressurized with nitrogen to run pressure, and the power was turned on to the heating system. During the pressurization period, the system was closely examined for gas leaks.

When system pressure was reached, a small bleed flow of nitrogen was allowed in order to purge the system of any oxygen that was present. This was done to minimize the potential and dangerous problem which exists when oxygen and hydrogen are present under pressure and at high temperatures. Care was taken to prevent high flowrates of nitrogen which could aspirate unreacted coal out of the hopper and into the product collection vessel. When the reactor had reached the desired run temperature, the nitrogen was turned off and hydrogen or hydrogen-hydrogen chloride was allowed to flow through the system. The flow rate was adjusted to the desired value by use of the micrometering valve and wet test meter.

At this time, ambient conditions were recorded and the feeder was started to commence the actual run. During the run, carrier gas flow-rate and reactor temperature were monitored continuously. Changes were made manually to keep these parameters at the desired run conditions. The carrier gas flow was adjusted with the micrometering valve and the reactor temperature was adjusted by varying the power

supplied by the powerstats to the heating system. Since the carrier gas was not preheated and the flow rates used were large, a significant change in temperature could occur due to a relatively small change in flowrate. Care was taken to insure that flowrates, and thus temperatures did not vary significantly.

The flowrate was measured downstream from the reaction system and it is assumed in this research that the hydrogen flow greatly exceeds the hydrogen consumed and/or the gaseous products produced. Thus the flowrate measured is essentially the total carrier gas flowrate. It should be noted that no attempt was made to evaluate either the extent or quality of the gases produced by the reaction.

After the run had been allowed to proceed for a designated period of time, usually one-half hour, the system was depressurized and the contents of the product collection vessel was removed and analyzed for conversion and for nitrogen and sulfur content.

I. Determination of Conversion

The determination of conversion was done on the basis of three solvent extractions. The product collected from the reactor was first extracted with cyclohexane yielding the oil product. The second extraction was done with toluene which yielded the asphaltene product, and the last extraction was done using pyridine yielding the asphaltol content of the product [7]. The total conversion was taken as the

sum of the three individual conversions. The extractions were made using the aid of a Soxhlet extraction apparatus (Figure 12).

The product removed from the product collection vessel was weighed to determine coal feedrate and then a portion was weighed and placed in a double thickness predried cellulose extraction thimble (40mm x 120mm). The thimble and sample were then placed in the extraction apparatus (Figure 12). The solvent vapor from the boiling flask rose through the side arm and up to the condenser where it condensed and fell into the thimble. When the solvent height reached the upper level of the siphon arm, it was siphoned through the thimble and back into the boiling flask. Any soluble material in the sample would then be carried with the solvent, through the thimble and back to the flask. The extraction procedure was allowed to progress until the solvent flowing through the walls of the thimble was clear.

The thimble and the sample residue were removed from the apparatus and allowed to air dry after each extraction was finished. The thimble was then placed in a drying oven at 100°C for twenty-four hours. If any product degradation or composition changes occurred as a result of this procedure, it is assumed to have been consistent as all samples were treated in a similar fashion. After the thimble was dried, it was weighed. This procedure was repeated for the same sample in the other two solvents. Unreacted coal was also analyzed for oil, asphaltene, and asphaltol conversion.

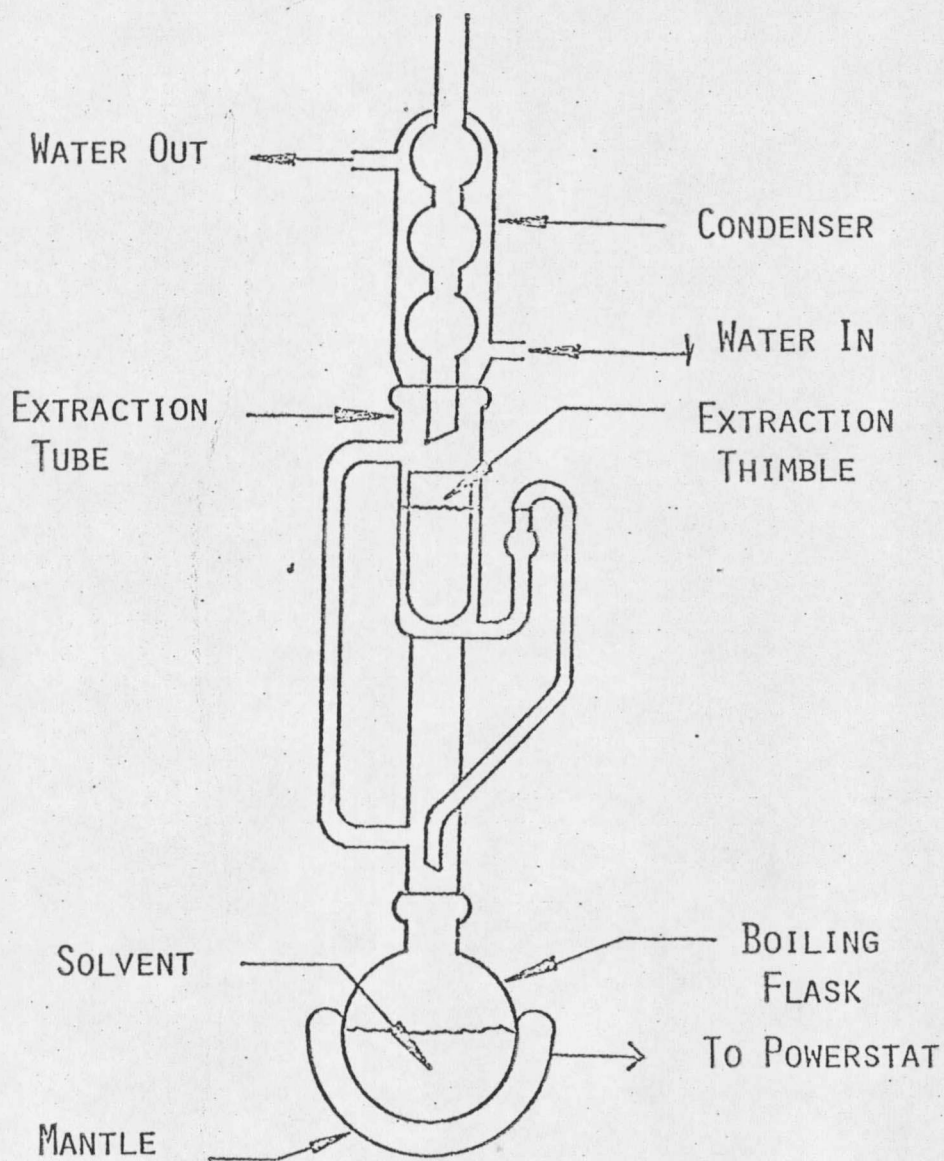


Figure 12. Soxhlet Extraction Apparatus Used to Determine Coal Conversion.

In making the conversion calculation, the difference in sample weights before and after the extraction was taken to be the amount of product converted to oil, asphaltene, or asphaltol. By knowing the ash, moisture, and catalyst content, the moisture, ash, and catalyst free (MACF) content of the original sample could be calculated. The weight loss by extraction would yield the conversion to the various products by the following equation:

$$C = (I/MAF) \times 100\% - V$$

or

$$C = (I/MAF) \times 100\% - V$$

for non-catalytic coals, where

- C = % conversion of coal to the respective product for each solvent,
- MAF = weight of moisture and ash from material present in the sample,
- MACF = weight of moisture, ash, and catalyst free material present in the sample,
- I = weight loss during extraction,
- V = percentage of solubles present in unreacted coal for that solvent.

The conversion then gives a representation of how the coal has been upgraded. The total conversion is the sum of the individual conversions for the same sample.

It is important to note here that the conversion to gaseous products was not studied. No means were taken to quantify the amount of gases produced in the reaction and only the conversion of liquid products is reported.

J. Sulfur and Nitrogen Determination

The products from all runs were analyzed for sulfur and nitrogen content as well as conversion to further characterize the activity of the catalysts.

Sulfur analyses were performed by the quartz tube combustion method using a Bico-Brown Shell design sulfur apparatus (ASTM D-1551) [39].

Nitrogen content was determined by the Macro-Kjeldahl method (ASTM E-258) [40]. The temperature of digestion was important in obtaining good reproducible results.

Sulfur and nitrogen content of the product oil and asphaltene were also determined for a few samples.

RESULTS AND DISCUSSION

A. Coal Analysis

Ash analysis was done at the beginning of this research on pulverized coal and used for calculation purposes throughout. The pulverized coal was assumed to be well mixed, as duplicate, randomly picked sample yielded reproducible results of 9.4 percent ash. This value corresponds closely with previous other literature reports for Rosebud coal [8, 41].

Coal was also analyzed for moisture content both before and after drying. The undried coal was found to have a moisture level of 20.1 percent. This again corresponds to literature values of 20.3 percent and 23.9 percent [7, 41].

Previous research has shown that pulverized coal shows a much greater tendency to feed uniformly when it has been predried [7, 19, 21]. In this research, guidelines set in a previous study were followed. The coal appears to reach an equilibrium drying time of forty-eight hours when kept in an oven at 100°C. This time was defined as when the time derivative of the coal weight change reached zero [7]. Water analysis on the dried coal showed that 0.5 percent moisture remained.

The storage, pulverizing and drying of the coal used in this research could have affected its ability to be liquified. Aging of coal has been shown to reduce its activity due to oxidation of the surface. Work done at the Bureau of Mines showed the coal aged four weeks in

the open environment dropped from 90 percent to 77 percent conversion. When the coal was dried at 105°C for one day, the conversion dropped to 54 percent. They also showed that the conversion was a function of the coal moisture content [42].

Other reports also show that coal will oxidize in air and change the amount of volatile matter available. The coal particle size is an important criteria for the accessibility of oxygen [7].

These trends show that both the drying and pulverization of the coal used in this research could have a detrimental effect on conversion. Both processes allow oxygen to be in contact with the coal. It is assumed, however, that if these effects are occurring, it will be consistent throughout since all samples were treated in a like manner.

Coal conversions were measured on the basis of three solvent extractions: cyclohexane, toluene, and pyridine. The products of the extractions are oil, asphaltene, and asphaltol respectively. This method of analysis was chosen due to its ability to more accurately describe the products of coal liquefaction [7, 9, 13, 14, 38]. Much of the basic research done on these solvent extractions was done using benzene in place of toluene. However, it has been shown that toluene can be substituted without any significant differences [12, 43].

Unreacted coal was tested for oil, asphaltene, and asphaltol content and was found to contain 0.4 percent oil, 0.2 percent asphaltene, and 0.1 percent asphaltol for a total of 0.7 percent total conversion.

No coal particle size distribution studies were done although it seems possible that this parameter could be optimized. It has been shown the coal conversion decreases with a decrease in the average particle size. This means that the smaller particles are carried through the reactor faster and thus are not in the hot zone long enough to be heated to reaction temperature [22]. It is also reported that coal can be fed more uniformly and reproducibly with smaller particle size coal [19, 22, 26].

B. Cold Flow Feedrate Tests

Since previous research at this University on the same experimental equipment resulted in very low and non-uniform coal feedrates, an attempt was made to understand this problem more fully. A comparison of the MSU operating parameters was done with another similar process operating at the University of Utah [22, 23]. This resulted in the premise that higher carrier gas flowrates were needed to obtain high coal feedrates. The University of Utah operated with a gas reactor residence time about ten times less than previous research done at MSU. The particle residence time is not the same as gas residence time due to friction and the tendency for partially liquefied, sticky coal particles to agglomerate and stick to the walls of the reactor.

This lead to a program to obtain coal feedrate data at various different carrier gas flowrates in which about 25 runs were made. These cold flow tests were done using operating conditions shown in Table III.

Table III. Cold Flow Testing Operating Parameters

Carrier Flow Gas	Nitrogen
Reactor Pressure	500 psig
Reactor Temperature	Ambient
Run Time	20 minutes
Coal Feed	-50 mesh
	dried
	catalytic

The results of these cold flow feedrate tests are shown in Figure 13. It can be seen that under these operating conditions, the coal feedrate increases uniformly with carrier gas flowrate. As a result of this test, it was decided to run at 30 scfh (standard cubic feet per hour) as a standard run condition.

Another operating variable was recognized as being affected by the change to increased carrier gas flowrate. Since the carrier gas was not preheated in this research, the laws of heat transfer predict that with increased flowrate, it will require more time for the gas to be heated to reaction temperature. A theoretical heat transfer analysis

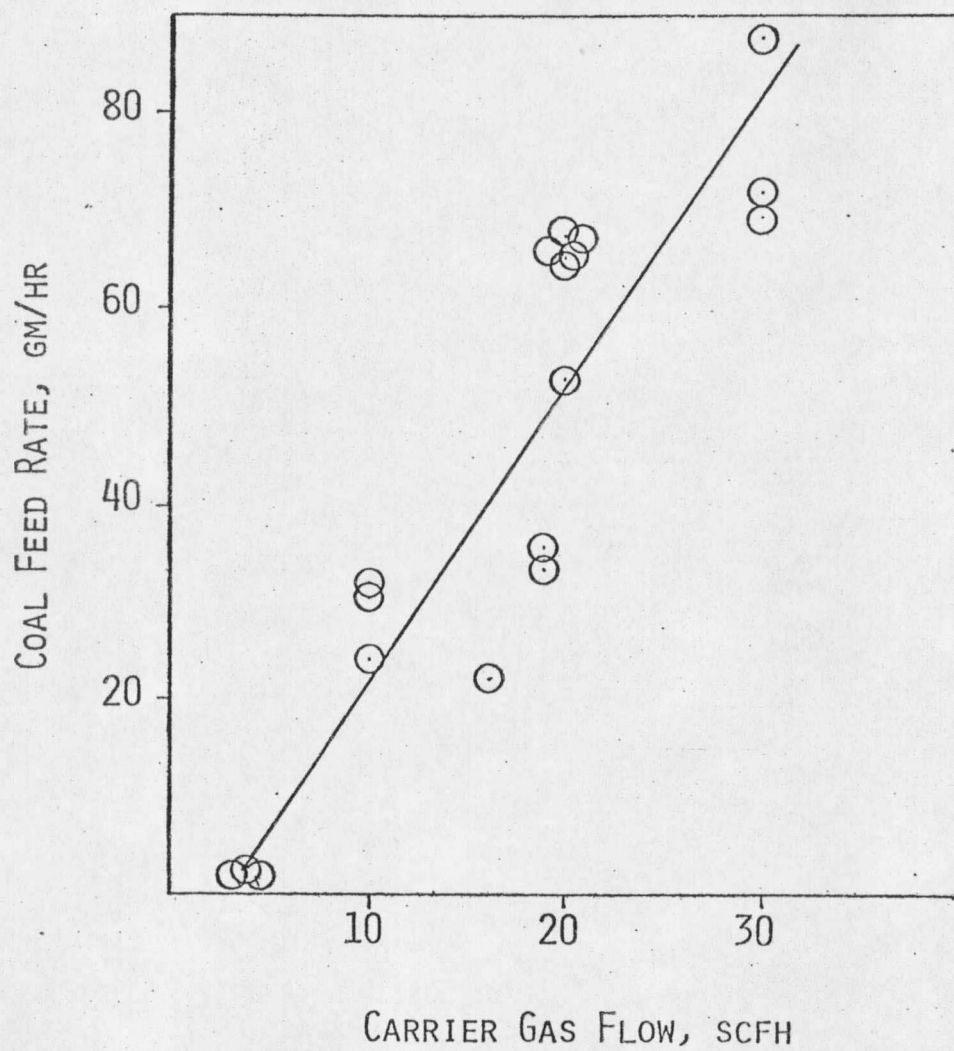


Figure 13. The Effect of Carrier Gas Flowrate on Coal Feedrate.

modeling the system as a double pipe heat exchanger with a heated length of six feet and a constant wall temperature of 500°C showed that the gas took up to half the length to be heated to reaction temperature. In practice, this model was conservative since the wall temperature would drop when high flowrates occurred. Thus the actual reaction temperatures are somewhat less than the temperature measured on the wall of the reactor.

C. Preliminary Research

Preliminary research was done to show that the equipment was operable at higher flow rates and to reproduce some previous data. The most important operating variable affected by the increased flowrate was the reactor temperature. Small changes in flowrate would cause the temperature to fluctuate from the desired run value. Frequent adjustments were required to keep the temperature close to the desired operating value.

Preliminary runs performed with non-catalytic coal using hydrogen as the carrier gas showed reproducibility of the coal feedrate and the viability of getting coal conversion at higher feedrates. Some preliminary run data is shown in Table IV. Table V shows the results of these preliminary runs.

Table IV. Some Preliminary Results

<u>Run</u>	<u>Avg. Run Temp. (°C)</u>	<u>Run Pressure (psig)</u>	<u>H₂ Flowrate (scfh)</u>	<u>Product Collection Rate (g/hr)</u>	<u>Total Conversion (%)</u>
E0*	---	---	---	---	0.7
E1	470	1,000	40	68	14.0
E2	450	1,000	38	68	11.9
E3	455	800	39	67	6.0
E4	460	1,000	26	19	7.2
E5	470	500	39	60	2.7

* E0 represents unreacted coal

Table V. Further Results of Preliminary Research

<u>Run</u>	<u>Conversion</u>			<u>%</u>	<u>%</u>
	<u>Oil</u>	<u>Asphaltene</u>	<u>Asphaltol</u>	<u>Sulfur</u>	<u>Nitrogen</u>
E0	0.4	0.2	0.1	.57	1.03
E1	13.1	0.6	0.3	.41	1.13
E2	9.0	2.1	0.8	.63	1.10
E3	5.8	0.1	0.1	.46	1.16
E4	6.7	0.4	0.1	.43	1.15
E5	2.1	0.5	0.1	.57	1.05

As a result of this research, the standard run conditions were chosen for the remainder of the research. These conditions were used in the catalytic screening research and were the basis of the work done to determine the effect of temperature, pressure and flowrate. In these tests, the variable being tested was altered from its standard condition. Table VI shows the standard run conditions.

Table VI. Standard Run Conditions

Temperature	500°C
Pressure	1,000 psig
Carrier Gas Flowrate	30 scfh
Reactor Length	6 ft
Coal Feed	-50 mesh
	impregnated catalytic
Run Time	30 minutes

D. The Effect of Catalysis on Coal Conversion

The six most active metal chlorides determined by Sire (1975) [37], along with non-catalytic coal were tested at standard conditions for coal conversion and product sulfur and nitrogen content. These catalysts were impregnated onto dried, pulverized coal from aqueous solution. To compare the catalysts on an equivalent basis, three per-cent metal on coal was chosen as the catalyst concentration. The catalysts used and coal catalyst concentrations are shown in Table VII.

Table VII. Metal Chloride Catalysts and Coal Concentrations

<u>Metal Chloride</u>	<u>% Metal on Coal</u>
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	2.86
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	2.20
ZnCl_2	2.97
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	2.83
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	3.20
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	2.40

The catalysts were impregnated by dissolving the equivalent amount of hydrated chloride such that the amount of metal would be 3 percent of 1,000 grams of coal. For hydrated nickel chloride, 121.5 grams were used to make the aqueous solution. All of the water was then driven off yielding the impregnated catalytic coal. The coal was then dried at 100°C to drive off all the water of hydration [7] and insure that the chlorides existed in the non-hydrated form.

The experimental runs were done in order of increasing catalyst volatility to minimize the effect of a highly volatile catalyst coating the reactor wall and affecting the subsequent runs.

The results of these catalyst tests along with the results of non-catalytic coal are shown in Table VIII for runs made with hydrogen at standard conditions. Table IX shows the conversions broken down into the individual fractions.

Table VIII. The Effect of Metal Chloride Catalysts on Coal Conversion

<u>Catalyst</u>	<u>Total Conversion</u>	<u>% Sulfur</u>	<u>% Nitrogen</u>
ZnCl ₂	24.0%	0.61	1.13
SnCl ₂	17.2%	0.55	1.10
CuCl ₂	16.5%	0.57	---
NiCl ₂	15.5%	0.52	1.14
CoCl ₂	10.8%	0.51	1.03
FeCl ₂	8.3%	0.61	1.00
Non-catalytic	4.2%	0.79	1.10
Unreacted Coal	0.7%	0.57	1.03

Table IX. The Effect of Metal Chloride Catalysts on Individual Coal Conversion

<u>Catalyst</u>	<u>Conversion</u>			<u>Total</u>
	<u>Oil</u>	<u>Asphaltene</u>	<u>Asphaltol</u>	
ZnCl ₂	16.9	6.1	1.0	24.0
SnCl ₂	14.3	2.9	0.0	17.2
CuCl ₂	13.0	2.8	0.7	16.5
NiCl ₂	14.0	1.5	0.0	15.5
CoCl ₂	9.9	0.9	0.0	10.8
FeCl ₂	5.7	1.9	0.7	8.3
Non-Catalytic	3.8	0.3	0.1	4.2
Unreacted	0.4	0.2	0.1	0.7

It is noted that all of the catalysts increase the coal conversion, up to a factor of six fold over non-catalytic coal.

Results of catalytic runs show conversions less than reported in previous catalytic studies using the same equipment [7]. The most probable reason for this is that the use of high flowrates in this research tended to reduce the actual reaction temperature from what was recorded. This lower conversion then apparently is a result of lower operating temperatures and not catalyst differences.

It appears that no desulfurization or denitrogenization is taking place. This could be because the liquefaction reaction is taking place at the outer surface of the coal particle and the product being analyzed is for the most unreacted coal. It can also be seen that the bulk of the conversion is in the oil fraction.

It has also been shown that as the percentage of catalyst in the coal increases from 1.5 to 6 percent metal on coal, the yield of asphaltene decreases significantly and the molecular weight of the asphaltene and hexane soluble oil decrease [45].

E. The Effects of Hydrogen Chloride on Coal Conversion

Each of the catalysts discussed in the previous section were run again, this time using a 5 percent mixture of hydrogen chloride in hydrogen as the carrier gas. The products were again analyzed for coal conversion and product nitrogen and sulfur content. The results

of these runs are shown in Table X. Table XI shows the hydrogen chloride catalyzed conversion broken down into the individual fractions.

As can be seen, in each case, the addition of 5 percent HCl to the feed gas results in a significant increase in total conversion. This data is consistent with previous batch coal hydrogenation studies [8, 37]. This data appears to follow the coal liquefaction mechanism proposed by Weller [44]. The thermal splitting of the coal apparently is catalyzed by the halogen acid, and these either polymerize to form insoluble products or are stabilized by the addition of hydrogenation to form soluble products. The hydrogenation appears to be catalyzed by the metal.

The increase in conversion here is significant. However, very little difference is seen for the various catalysts. This could be due to the HCl catalyzed reaction being the rate limiting step. Note that even the non-catalytic coal was increased significantly due to the addition of HCl alone. By comparing data in Table IX and XI, it is noted that most of the increase in conversion comes in the most desirable oil fraction.

Table XII presents the nitrogen and sulfur contents of the products of runs performed with hydrogen chloride. Again no desulfurization or denitrogenation appears to have taken place. Again, it is plausible that the analyzed product is for the most part unreacted coal, indicating that the reaction occurs on the outer coal surface.

Table X. The Effect of Hydrogen Chloride on Coal Conversion

<u>Catalyst</u>	<u>Total Conversion H₂</u>	<u>Total Conversion H₂-HCl</u>
CoCl ₂	10.8	44.2
SnCl ₂	17.2	38.3
CuCl ₂	16.5	37.8
NiCl ₂	15.5	37.6
ZnCl ₂	24.2	34.3
FeCl ₂	8.3	34.2
Non-catalytic	4.2	25.0

Table XI. The Effect of Hydrogen Chloride On Individual Coal Conversion

<u>Catalyst</u>	<u>Conversion</u>			<u>Total</u>
	<u>Oil</u>	<u>Asphaltene</u>	<u>Asphaltol</u>	
CoCl ₂	29.7	12.6	1.9	44.2
SnCl ₂	33.3	4.1	0.9	38.3
CuCl ₂	33.2	3.7	0.9	37.8
NiCl ₂	34.2	2.9	0.5	37.6
ZnCl ₂	31.9	2.4	0.0	34.3
FeCl ₂	29.9	4.3	0.0	34.2
Non-Catalytic	20.6	3.5	0.9	25.0

Table XII. Nitrogen and Sulfur in HCl Runs

<u>Catalyst</u>	<u>% Sulfur</u>	<u>% Nitrogen</u>
CoCl ₂	0.67	1.34
SnCl ₂	0.53	0.97
CuCl ₂	0.36	0.98
NiCl ₂	0.52	1.00
ZnCl ₂	0.39	1.04
FeCl ₂	0.56	1.03
Non-catalytic	0.29	---
Unreacted coal	0.57	1.03

F. The Effect of Temperature on Coal Conversion

As shown by Figure 14, the coal conversion increased rapidly with increasing temperature. Temperatures used were 600, 500, and 400°C using hydrogen as the carrying gas and nickel chloride catalyzed coal.

This can be explained by the postulated mechanism of coal hydrogenation [44]. Coal is split thermally to form reactive fragments. It is plausible that at lower temperatures, there is insufficient thermal energy to split the coal thus producing less molecular fragments. This then would reduce the number of active sites available for

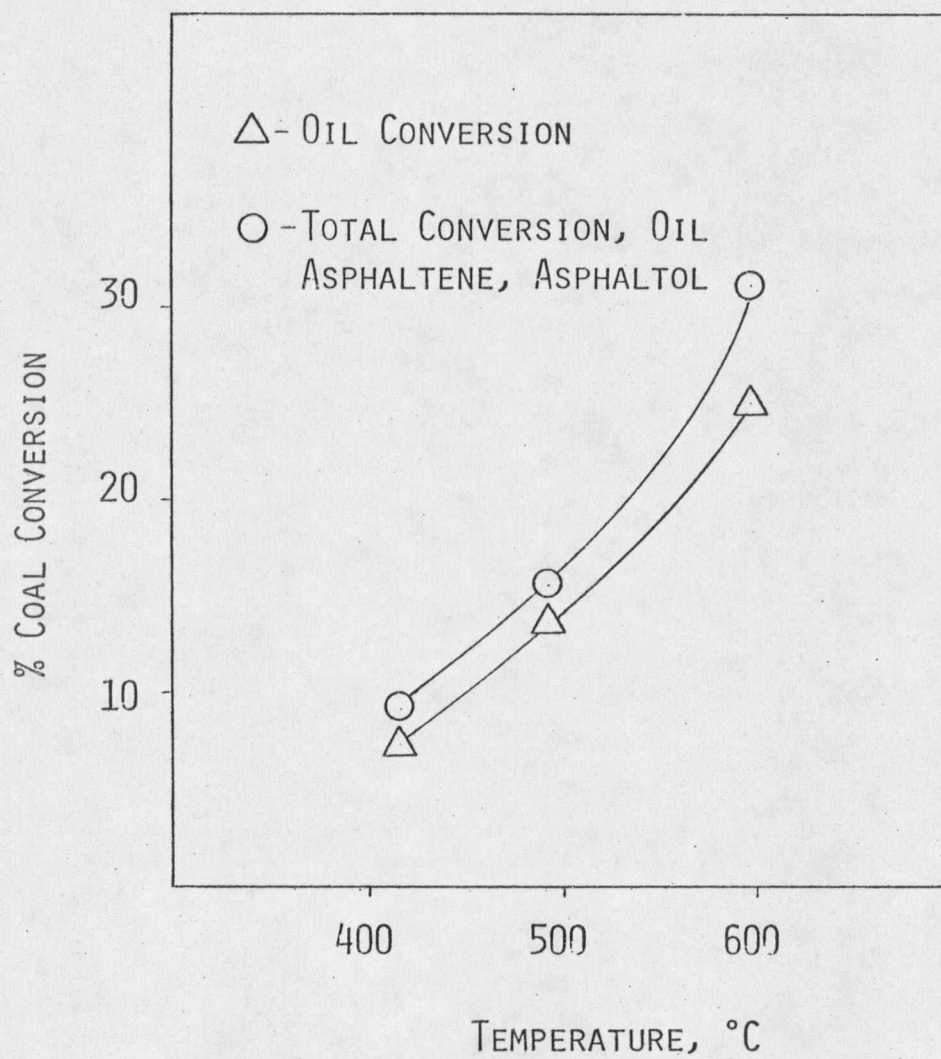


Figure 14. The Effect of Temperature on Coal Conversion.

stabilization into soluble products by the addition of hydrogen. This trend is supported by data frequently reported in the current coal liquefaction literature [7, 8, 22]. Wood and Wiser report 700°C is required to achieve 65 percent conversion, while Biegalko reports non-catalytic conversion to be over 30 percent at 600°C.

G. The Effect of Carrier Gas Flow Rate on Coal Conversion

As shown by Figure 15, the coal conversion decreases with increasing carrier gas flowrate. The carrier gas used in this investigation was hydrogen, while nickel chloride catalytic coal was used. Hydrogen flowrates tested were 9, 14, and 30 standard cubic feet per hour. This trend would be expected since an increase in hydrogen flowrate, or linear velocity through the tube, also would reduce the coal residence time in the reaction zone. This trend is also reported by Wood and Wiser using similar equipment [22]. They also report a coal particle residence time of two to six seconds for a one-half inch reactor tube which compares with a gas residence time of 0.8 seconds for the same situation. This seems to indicate that coal sticks to the hot tube wall to some extent.

The gas residence time for the various flow rates are present in Table XIII, based on six feet of heated reactor length.

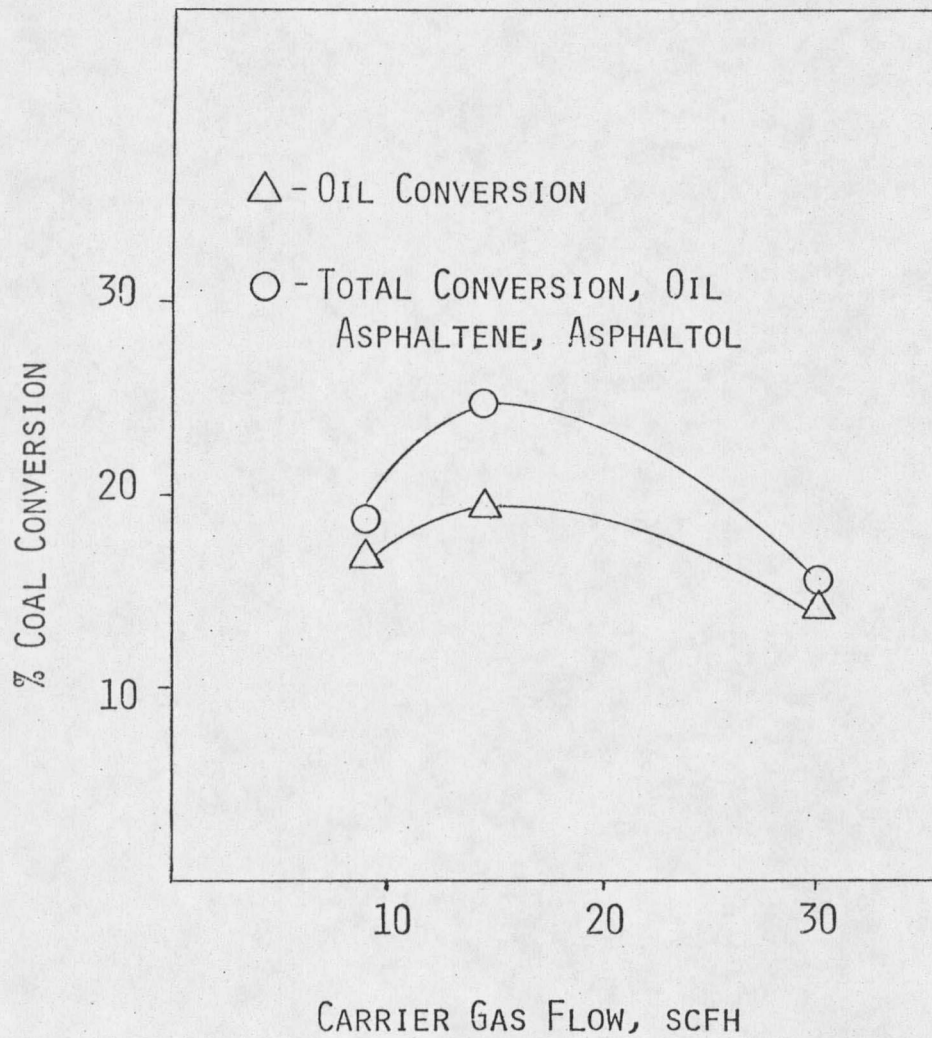


Figure 15. The Effect of Carrier Gas Flowrate on Coal Conversion.

Table XIII. Reactor Gas Residence Time

<u>Hydrogen Flow Rate</u> (scfh)	<u>Residence Time</u> <u>For Six Foot Reactor, Sec.</u>
9	0.19
14	0.12
30	0.06

H. The Effect of Pressure on Coal Conversion

The effect of pressure on coal conversion is shown on Figure 16. As noted, the conversion drops sharply with decreasing pressures. Pressures tested were 1,000, 800, and 500 psig. Nickel chloride catalytic coal was used with hydrogen as the carrier gas. This trend is also verified frequently in the literature and is plausible since the use of increased pressure intensifies the availability of hydrogen to react with fragmented molecules [7, 22, 23, 28].

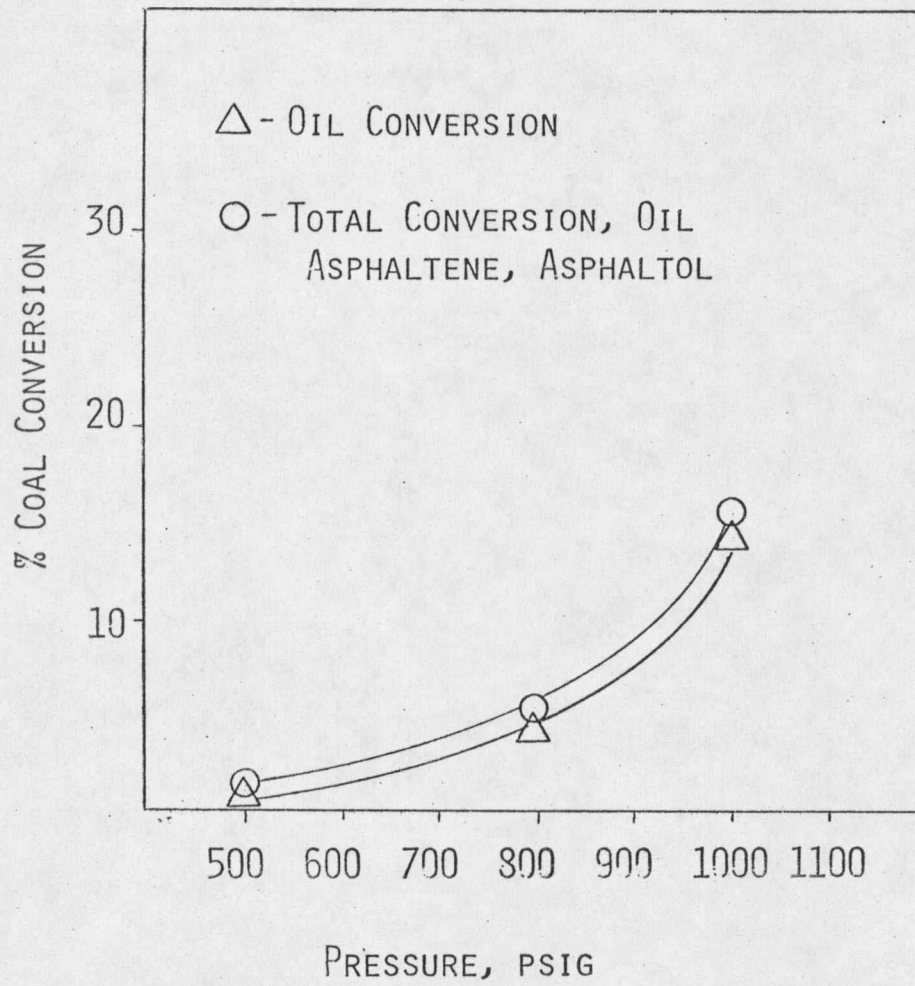


Figure 16. The Effect of Pressure on Coal Conversion.

I. Sulfur and Nitrogen Content of Oil and Asphaltene Fractions

To further characterize any denitrogenation and/or desulfurization which took place during the reaction, sulfur and nitrogen content of the oil and asphaltene product of selected runs were determined. Since the oil and asphaltene fractions were extracted into a solvent, they were further isolated to be analyzed. This was done by boiling off the solvent until a weight ratio of about three parts solvent to one part oil or asphaltene remained. Thus, this is the sample that was analyzed for sulfur and nitrogen. The results are shown in Table XIV. It can be noted that the appearance of desulfurization and denitrogenation of the oil and asphaltene products probably occurs. Note that the data reported represents the nitrogen and sulfur of three to one ratio of solvent to product and the volumetric means of deriving this sample was approximate.

Table XIV. Sulfur and Nitrogen Content of Oil and Asphaltene

Fractions		
<u>Fraction</u>	<u>Sulfur</u>	<u>Nitrogen</u>
G14 Oil	0.09	0.011
G15 Oil	0.075	0.016
G16 Oil	0.16	0.008
G14 Asphaltene	0.10	0.012
G15 Asphaltene	0.14	0.009
G16 Asphaltene	0.07	0.011
G17 Asphaltene	0.15	0.012

CONCLUSIONS

The following conclusions can be made:

- (1) Pulverized coal is a difficult medium to feed uniformly and reproducibly at high pressures.
- (2) Unreacted coal contains 0.4 percent oils, 0.2 percent asphaltenes, and 0.1 percent asphaltols for a total conversion of 0.7 percent.
- (3) The coal feedrate is a function of carrier gas flowrate under the operating conditions used in this thesis work.
- (4) Conversion of coal into characterizable liquid products can be made using rapid coal liquefaction methods.
- (5) Impregnated metal chloride catalytic coal yields higher conversions under similar operating conditions than non-catalytic coal.
- (6) The addition of hydrogen chloride to the carrier gas hydrogen stream results in a significantly higher conversion for both metal chloride catalyzed and non-catalyzed coal.
- (7) The nitrogen and sulfur content of the solid product analyzed remain virtually unchanged from unreacted coal.
- (8) Increases in temperature increase the coal conversion attained with catalytic coal.
- (9) Increases in carrier gas flowrate decrease the coal conversion attained with catalytic coal.

(10) Increases in system pressure increase the coal conversion attained with catalytic coal.

(11) Denitrogenation and desulfurization are evident in the oil and asphaltene fractions of the liquid products.

RECOMMENDATIONS FOR FUTURE STUDY

Due to the operating problems encountered with the present experimental apparatus in this thesis work, several major modifications are suggested before attempts are undertaken to obtain any more experimental data. Operating problems such as coal feeder plugging, extreme temperature variations, and reactor plugging resulted in the making of 2.5 times as many experimental runs as reported herein.

Equipment changes that are recommended are:

- (1) Install a hydrogen (carrier gas) pre-heating system. In virtually all similar research which is presently being conducted around the country, a hydrogen pre-heating system is used. This could be done by building a heating system similar to the one presently used to heat the reactor. A length of coiled tubing wrapped around an internally heated steel pipe located directly upstream of the hydrogen inlet of the coal feeder would seem to do the job. Care should be exercised to insure that the pre-heat system heat input is significantly oversized so large heat transfer rates due to changes in large flowrates do not affect the reactor temperature.
- (2) Install a product quench system. Again, current research indicates that a quenching system be used to minimize the

time the products of coal liquefaction are exposed to high temperatures. This quench could be done by injecting a cold flow of hydrogen or nitrogen into the reactor system just downstream from the reactor outlet. Bathing the product collection vessel in water would not be a suitable method of quench since the manufacturer of that piece of equipment indicates that loss of structural integrity may occur in that situation.

- (3) Install larger diameter reactor tubing. The use of larger diameter tubing would help both the heat transfer problem encountered and also tend to reduce the problems encountered with reaction plugging. It is recommended that the outside diameter be a minimum of 5/16" with 3/8" tubing desired.
- (4) Install a product condensing system. This thesis work has determined that a product condensing system is imperative if future work is to generate more meaningful data. It is believed that presently much of the liquid product is passing through the product collection vessel as a vapor. Evidence of this is the fact that a tarry liquid substance can be found inside the process lines and pressure regulator downstream from the collection vessel. Additional evidence is the formation of an oily layer in the exit gas scrubber. It is

recommended that a second product collection vessel be added to the flow system mounted below a vertical water condenser.

New experiments that are recommended include:

- (1) Characterization of condensed liquid products by conversion methods and sulfur and nitrogen methods outlined herein.
- (2) Analysis of exit gas stream by gas chromatography. This would probably require the use of a pressurized flow meter upstream of the reactor to measure carrier gas flowrates. Gas chromatography methods are reported by other institutions performing similar research.
- (3) Test the effect of a hydrocarbon vehicle on product conversion. Vehicles such as propylene, penetech oil, decaline, toluene, and tetraline could serve as a hydrogen donor and have been shown to be effective in similar previous batch studies.
- (4) Examine the recoverability of the catalyst used so the catalyst economics can be studied.
- (5) Characterize liquid products by ASTM distillations. Longer run times may be needed to generate adequate amounts of product.

- (6) Run with other halogens in the gas feed such as boron tri-fluoride and hydrogen flouride.
- (7) Run using solid SRC rather than coal for the feed material.
- (8) Determine the effect of catalyst concentration on coal conversions and process economics.
- (9) Determine the effect of HCl concentration in the feed gas on coal conversion, product denitrogenation, and process economics.
- (10) Determine the effect of higher pressures on coal conversion.

APPENDIX

Table XV. Typical Run Data

RUN F-6

Run Conditions

Temperature	500°C
Pressure	1,000 psig
Flowrate	30 scfh
Feeder Setting	10
Coal Feed	Copper Catalyzed, -60 mesh, dried
Carrier Gas	H ₂
Barometer	639.3
Ambient Temperature	73°F

<u>Time</u> (Min.)	<u>Flowrate</u> (Sec/rev)	<u>Temperature</u> (°C)	<u>Remarks</u>
0	7.4	480	Start
5	8.4/7.7	500	OK
11	8.0	510	
21	8.3/7.8	490	
29	8.1	510	Backoff Heat
38	8.0	500	
46	8.1	490	
53	8.2	500	
<u>60</u>	<u>8.0</u>	<u>510</u>	Shutdown
60 min.	8.0 Avg.	499 Avg.	

$$\text{Flowrate} = \frac{360}{8.0} \times \frac{492}{760} \times \frac{639.3}{534} = 35 \text{ scfh}$$

Table XVI. Results of Preliminary Research

Run No.	Avg. Run Temp. (°C)	Run Pressure (psig)	Avg. Run Gas Flowrate (scfh)	Avg. Product Collection Rate (g/hr)	Conversion %		
					Oil	Asphaltene	Asphaltol
E1	470	1,000	40	68	13.1	0.6	0.3
E2	450	1,000	38	68	9.0	2.1	0.8
E3	455	800	39	67	5.8	0.1	0.1
E4	460	1,000	26	19	6.7	0.4	0.1
E5	470	500	39	60	2.1	0.5	0.1

TABLE XVII. Final Run Data, Operating Parameters

Run No.	Avg. Run Temperature (°C)	Run Pressure (psig)	Avg. Run Gas Flowrate (scfh)	Carrier Gas	Product Collection Rate (g/hr)	Catalyst
F1	480	1,000	35	H ₂	30	None
F2	501	1,000	37	H ₂ HCl	20	None
F3	508	1,000	37	H ₂ HCl	7	CuCl ₂
F6	499	1,000	35	H ₂	3	CuCl ₂
F7	491	1,000	35	H ₂ HCl	3	CoCl ₂
F11	486	1,000	36	H ₂	3	ZnCl ₂
G6	494	1,000	36	H ₂	51	FeCl ₂
G7	504	1,000	30	H ₂ HCl	15	FeCl ₂
G8	515	1,000	30	H ₂ HCl	10	ZnCl ₂
G9	505	1,000	30	H ₂	34	CoCl ₂
G10	503	1,000	30	H ₂ HCl	33	SnCl ₂
G12	491	1,000	30	H ₂	29	SnCl ₂
G14	498	1,000	30	H ₂ HCl	35	NiCl ₂
G15	491	1,000	30	H ₂	22	NiCl ₂
G16	416	1,000	30	H ₂	15	NiCl ₂
G17	508	1,000	9	H ₂	6	NiCl ₂
G18	500	1,000	14	H ₂	16	NiCl ₂
G19	593	1,000	30	H ₂	22	NiCl ₂
G20	495	800	30	H ₂	27	NiCl ₂
G21	501	500	30	H ₂	15	NiCl ₂

Table XVIII. Final Run Data, Conversions

Run No.	Conversion %			Total	% Sulfur	% Nitrogen
	Oil	Asphaltene	Asphaltol			
F1	3.8	0.3	0.1	4.2	0.79	1.10
F2	20.6	3.5	0.9	25.0	0.29	--
F3	33.2	3.7	0.9	37.8	0.36	0.98
F6	13.0	2.8	0.7	16.5	0.57	--
F7	29.7	12.6	1.9	44.2	0.67	1.34
F11	16.9	6.1	1.0	24.0	0.54	1.13
G6	5.7	1.9	0.7	8.3	0.61	1.00
G7	29.9	4.3	0.0	34.2	0.56	1.03
G8	31.9	2.4	0.0	34.3	0.39	1.02
G9	9.9	0.9	0.0	10.8	0.51	--
G10	33.3	4.1	0.9	38.3	0.53	0.97
G12	14.3	2.9	0.0	17.2	0.55	1.10
G14	34.2	2.9	0.5	37.6	0.52	1.00
G15	14.0	1.5	0.0	15.5	0.62	1.14
G16	7.5	1.3	0.4	9.2	0.62	1.08
G17	16.4	1.8	0.5	18.7	--	--
G18	19.1	4.9	0.8	24.8	0.54	1.26
G19	25.6	5.1	0.6	31.3	--	0.86
G20	4.3	0.8	0.2	5.3	0.64	1.00
G21	1.3	0.4	0.0	1.7	--	1.16

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